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Release and phytoavailability of phosphorus in soils treated with phosphate rocks and organic acids

Kokoasse Kpomblekou-Ademawou
Iowa State University

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Kpomblekou-Ademawou, Kokoasse, Ph.D.

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U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

Release and phytoavailability of phosphorus in soils treated with phosphate rocks and organic acids

by

Kokoasse Kpomblekou-Ademawou

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DEDICATION

This thesis is dedicated to my mother Akouélé Kpomblékou who has given me all she had and taught me to understand that a fish never drowns but always swims even in strong currents, to my late father Govina Kpomblékou who passed away during my struggles abroad to make his dreams come true; may his soul rest in peace and may God give me his courage and bravery to continue his good work, to my brother Mawulé Vovoti Kpomblékou for providing me the guidelines during all these years, to my sisters Lawoê and Diavo for their love, to my lovely wife Akouavi D. Kpomblékou née Sossou and my lovely and wonderful daugthers Séfako and Madjé Kpomblékou for joining me on this long journey of achievements.

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INTRODUCTION

The genetic role of phosphorus (P) in ribonucleic acid and its function in energy transfers via adenosine triphosphate (ATP) have made P one of the most indispensable elements for all forms of life. Phosphate compounds in the plant system act as "energy currency" that power almost any biological process in plants. Besides the metabolic role of P in the plant life cycle, phosphorus is a vital structural component of nucleic acids, nucleotides, coenzymes, sugar phosphates, phospholipids, and phosphoproteins (Tisdale et al., 1985). Among the 17 essential elements found in plants, P appears to be the most limiting element; it cannot be released from organic residues nor be recycled in rainfall (Ozanne, 1980). Adequate supply of P in the early stages of plant growth improves root growth and speeds up the formation of reproductive organs. Strength of cereal straw, quality of fruits, vegetables and forages are associated with adequate P levels in soils.

Phosphate species are the main forms of P in the environment. For convenience, P will be used throughout this dissertation to refer to phosphate-P. Adequate P nutrition also increases tolerance of grains to root-rot diseases and improves disease resistance. Early maturity of grain crops and reduction in ripening time required for grain are also associated with P nutrition. Phosphorus deficiency severely retards plant growth, root proliferation and deeply disturbs all metabolic processes in plants and must be restored only by addition of available P as a fertilizer (Tisdale et al., 1985). The absence of P prevents other nutrients from being taken up by plants. Nitrogen

uptake for instance is indirectly dependent on P supply and no single nitrogen fixing legume can efficiently use N without P. The amount of total P in mineral soil is low; about 90 to 2225 lb $acre^{-1}$ with an average of 890 lb $acre^{-1}$ in the top 8 inches (Tisdale et al., 1985). Only part of this total amount is available to plants. Although P nutrition is critical in soil fertility management, only four sources of P have the potential to meet P demand: (1) native organic and inorganic compounds of P already present in soil, (2) animal manures, (3) plant residues, and (4) commercial fertilizers. Inorganic and organic forms of P are both important sources. The inorganic sources contain Ca or Fe and Al; the most common calcium compounds found in soils are: fluorapatite ($3Ca_3(PO_4)_2.CaF_2$), Carbonate apatite ($3Ca_3(PO_4)_2.CaCO_3$), hydroxyapatite ($3Ca_3(PO_4)_2.Ca(OH)_2$), oxyapatite ($3Ca_3(PO_4)_2.CaO$), tricalcium phosphate ($3Ca_3(PO_4)_2$) dicalcium phosphate ($CaHPO_4$), and monocalcium phosphate ($Ca(H_2PO_4)_2$). Less is known, however, about Al and Fe phosphates (variscite, strengite, wavellite and dufrenite), which are very stable and insoluble in acid soils (Brady, 1974). Three main forms of organic P compounds are found in soils: phospholipids, phytin and nucleic acids. Inorganic soil P compounds are extremely insoluble (exceptions are mono and dicalcium phosphate) and their availability primarily depends on soil pH, amount of soluble Fe, Al and Mn, available Ca, amount of organic matter present, and microbial activity. Organic P compounds in soils can be utilized as P sources, but their availability is also questionable. Animal manures contain relatively low concentration of P in comparison with commercial fertilizers;

only about one fifth of P present may become available to the first crop (Brady, 1974) and only a small portion of P from crop residue is available for plant uptake. The only important source of available P in soil is commercial P fertilizers. About a dozen phosphorus carriers are manufactured: superphosphates, ammoniated superphosphate, ammonium phosphate, ammonium polyphosphate, diammonium phosphate, nitric phosphates, steamed bone meal, phosphate rock, calcium metaphosphate, phosphoric acid, superphosphoric acid, partially acidulated phosphate rock, potassium phosphate, dicalcium phosphate, and bacterial phosphate fertilizers (Brady, 1974).

The primary source of P in manufactured phosphatic fertilizer was bones; after rapid exhaustion of bone supply, the only source of almost all manufactured phosphate fertilizers became phosphate rock.

Phosphate rock (PR) is referred to as any naturally occurring apatite-bearing rock that contains P in a concentration high enough to be used to produce P fertilizer. Such deposits occur in almost every place in the world (Continent and Islands), but only few carry some economic importance. The world production of PR in 1990 reached 152,833 metric tons (Mew, 1991). Over 30 countries produce PR. These are: Finland, Sweden, Turkey, The former U.S.S.R., Algeria, Egypt, Morocco, Senegal, South Africa, Tanzania, Togo, Tunisia, USA, Brazil, Columbia, Mexico, Peru, Venezuela, Iraq, Israel, Jordan, Syria, India, Pakistan, Christmas Island, China, Korea (D.P.R.) Vietnam, Australia, and Nauru (Mew, 1991). The problem related to the use of conventional P fertilizers is threefold: (1) rapid conversion of phosphorus into

nonavailable forms (this is especially true in soils rich in Fe and Al oxides with high P fixing capacity), (2) continuous increase in P fertilizer cost which limits the use of P fertilizer, especially in developing countries which can no longer afford to subsidize fertilizers, and (3) public awareness in environmental concern about heavy metals introduced into soils via P fertilization. All these three points have to be addressed and solutions must be found. There is considerable evidence on accumulation of heavy metals in soils as a result of P fertilization application (Mortvedt, 1987). However, heavy metal uptake by plants remains a matter of controversy. One solution to controlling the increasing cost of P fertilizers and the P fixation problems is to use of nonconventional P fertilization with slow P release into soil solution. Several approaches have been employed to control these problems. These include the use of partially acidulated phosphate rocks and the use of compacted PR with water-soluble P fertilizers (Kpomblekou et al., 1991). However, little information is available on the use of organic acids to enhance P release from PR. Low-molecular-weight organic acids are produced naturally in soils through microbial activities. Several of these acids have the ability to complex Al, Ca, Fe, Mg, Mn, and Zn by ion-exchange, surface adsorption, coagulation and peptization reactions and, therefore, play an important role in the mobilization of such metals in soil-water systems. These complexation reactions may lead to the release of P from P-bearing minerals. Therefore, the objectives of this study were: (1) to quantify trace and nontrace metal content of PRs, (2) to evaluate P release from phosphate rocks by several organic and mineral

acids, (3) to evaluate the influence of free carbonate content on P release from phosphate rocks by selected organic and sulfuric acids, (4) to study the P release from phosphate rocks mixed with organic acids and added to soils under laboratory conditions, and (5) to assess the phytoavailability of phosphorus in soils treated with phosphate rocks and organic acids. For convenience, the results are presented in four parts. Part I includes the results obtained under objective (1), Part II includes those obtained under objectives (2) and (3), Part III includes those obtained under objective (4) and Part IV includes those obtained under objective (5).

LITERATURE REVIEW

Even though the first description of phosphate rock (PR) appeared in Eastern Portugal in 1782, it was not until 1829 when the first detailed study on PR was completed by William Buckland (Cook et al., 1990). Liebig was the first to suggest that PR or phosphorite could be used as fertilizer in the same manner as bone and guano (manure of sea birds). The material was sold as "coprolite manure" to farmers. John Lawes dissolved phosphate rock in sulfuric acid producing a more soluble product and patented the process in 1842 for chemical production of the material. This marked the beginning of phosphate industry. Soon several phosphate deposits were discovered in France, Belgium, Eastern Europe, Russia, North America, North Africa (Tunisia, Algeria and Morocco) and elsewhere (Cook et al., 1990).

A number of hypotheses exist on the origin of PR; they all recognize a relationship between the biota and PR depositions. One of the early hypotheses suggested that mass mortality of fish was the cause of phosphate rock formation; the reason for this mass mortality was not understood, however. Another hypothesis involves the idea of direct precipitation of apatite from marine bottom. Today, the generally accepted hypothesis suggests that PR deposition was a consequence of interaction of several factors such as oceanography, plate tectonics and sea-level (Cook et al., 1990); the role of bacteria in phospho-genesis is also recognized.

Early studies on PR were carried out to determine the best cropping and soil factors that are favorable for PR use (Hammond et al., 1986). The results obtained

were conflicting and confusing. These differences in results are related to the mineralogical composition of PR.

Mineralogy and Chemistry of Sedimentary Apatites

The trade name phosphate rock, consists of a complex assemblage of phosphate and other minerals. The most common phosphate minerals belong to the apatite family. Apatite in PR has three origins (metamorphic, igneous, and sedimentary) and varies considerably in mineralogical composition, physical, chemical, and crystallographic properties. The principal constituent of metamorphic and igneous PRs is fluorapatite: $Ca_{10}(PO_4)_6F_2$, whereas carbonate fluorapatite (francolite) is usually found in sedimentary rocks (McClellan and Lehr, 1969). Sedimentary apatites with fluorine content higher than 1% are designated francolite (McConnell, 1938). Sedimentary apatites differ greatly in composition from pure fluor- and hydroxy-apatites; they are microcrystalline and have considerable substitution of carbonate for phosphate and other metals for Ca. Sedimentary apatites also nearly always contain more F than is required by the empirical formula $Ca_{10}(PO_4)_6F_2$; it has been assumed to be present as fluoride in crystals too small to be detected by x-ray diffraction or petrography (McClellan and Lehr, 1969). The mode of occurrence of this excess F in sedimentary apatite structure is not clear, however. Chemical studies suggested that a carbonate ion replaces a tetrahedral phosphate ion in the apatite lattice and the vacant oxygen site is occupied by an F ion (Borneman-Starinkevich and Belov, 1953). This carbonate-fluorine ion arrangement is unusual; it would have no mutual bonding, but would

preserve electroneutrality and complete the coordination of the cations in the structure. Work by Elliott (1964), Smith and Lehr (1966), Gulbrandsen (1966), and Trueman (1966) supported Borneman-Starinkevich's and Belov's (1953) theory. Trautz (1960) provided evidence that the carbonate occupied the place of the two phosphate tetrahedrons mutually inclined to the c axis.

In 1969, McClellan and Lehr investigated the mineralogy and composition of 110 francolites and igneous apatites. Their results showed good correlations between crystallographic properties and chemical composition of the apatite fraction of the rocks. The data also suggested that the carbonate for phosphate substitution took place in 1 to 1 ratio, and that as the degree of carbonate for phosphate substitution increased the length of a and b axes changed. Moreover, they noted an increase in c and a decrease in unit-cell a dimensions as a result of the increasing substitutions. In addition, their chemical data suggested that not all, but only part of the carbonates that replace phosphates, are accompanied by fluoride; the resulting electrical unbalance was corrected by substitution of Na and Mg for Ca. Based on the assumptions that the basic substitution is carbonate for phosphate and that electroneutrality must be preserved, McClellan and Lehr (1969) idealized the general formula for sedimentary apatites:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{2+0.4x}.$$

Recently, McClellan and Kauwenbergh (1990) investigated 260 francolite samples including only the francolite portion of the database used by McClellan and

Lehr (1969). The samples thus investigated did not contain any igneous, guano, lacustrine or insular samples. They found a linear relationship between the moles of carbonates and phosphates per unit cell substitution, confirming earlier findings in the isomorphic substitution of carbonates for phosphates on a 1:1 basis. They reported a limit of substitution of 1.5 moles per unit cell, whereas McClellan and Lehr (1969) calculated a maximum substitution of 1.395 moles. Post-depositional alteration may account for the extent of the carbonate substitution. McClellan and Kauwenbergh (1990) also observed that when about 25% of the phosphate is substituted for carbonate, about 6% of the Ca is replaced by Na and Mg, making Na an important element in the achievement of electroneutrality in the apatite structure. The reason for Mg substitution is not understood because it has the same valence as Ca; perhaps Mg is needed to compensate for other substitutions. There are also reports on other substitutions (to a lesser degree) of SO_4^{2-}, SiO_4^{2-}, AsO_4^{3-}, VO_4^{3-}, CrO_4^{2-}, and AlO_3^{3-} and of F^- for OH^- and Cl^- for phosphate (Lehr, 1967; McClellan and Lehr, 1969; Lehr and McClellan, 1972). These substitutions affect in measurable ways the crystallographic properties, namely unit-cell parameters and optical indices. These properties can be examined by chemical analysis, petrographic microscopy, x-ray powder diffraction, infrared spectroscopy, and electron microscopy. By chemical analysis, Lehr (1967), McClellan and Lehr (1969), Lehr and McClellan (1972) showed that among more than 25 elements reported to be present in apatite only six have great importance: Ca, Mg, Na, P, CO_2, and F. Maslennikov and Kavitskaya (1956) used the x-ray diffraction

technique to determine the phosphate substitution of some phosphorite samples and reported measurable changes in the unit-cell a dimensions with changes in carbonate content of these samples. Smith and Lehr (1966) were the first to establish a relationship between mineralogical compositions and reactivity of apatite using x-ray diffraction technique to characterize 55 samples from 47 deposits. The studies showed reasonable correlation between the total F content, the carbonate content, and the length of the a and c axes. The researchers pointed out however, that the a-value was the most affected by the isomorphic substitution. McClellan and Lehr (1969) reported values of a from 9.322 to 9.409 Å and values of c from 6.876 to 6.901 Å. The x-ray diffraction technique is by far the most accurate method for determining the apatite composition of PR, but it requires sophisticated instrumentation (Lehr et al., 1967). Infrared characterization and petrographic examination are rapid methods used to approximate apatite composition of PRs.

There has been a growing interest in direct application of PRs; it was, however, observed that the availability of P in PR for crop is directly related to phosphate-bound carbonates, which are different from carbonates of accessory calcite and dolomite (Caro and Hill, 1956). Greenhouse experiments and numerous field trials demonstrated that the effectiveness of PR is directly related to the degree of carbonate substitution for phosphate in the apatite structure. The substitution therefore has tremendous effect on PR solubility. Arminger and Fried (1957) and Terman et al. (1970) showed that the agronomic effectiveness of PR is related to its reactivity (rate of P release under

favorable soil conditions), and that laboratory methods can be designed to measure the value of a PR as fertilizer for direct application. Several methods have been designed for predicting the reactivity of PR, including extraction of P with: (1) neutral, normal ammonium citrate (AOAC, 1970), (2) 2% citric acid (Arminger and Fried, 1957) used in Brazil, (3) 2% formic acid (Hoffman and Mager, 1953) used in the European Common Market, (4) 1% lactic acid, (5) Na-EDTA, and (6) ^{32}P exchangeable P. None of these methods, however, has been standardized; they yield large differences that may cause confusion in interpretation of the data (McClellan and Gremillion, 1980). The P extracted by neutral normal ammonium citrate solution is underestimated because part of the solution is consumed by the accessory gypsum, calcite or dolomite. On the other hand, the portion of P extracted by 2% citric acid is overestimated because of the presence in the rock of acid-soluble Al phosphate (Lehr and McClellan, 1972; McClellan and Gremillion, 1980). Moreover, some other studies showed that 2% citric acid and 2% formic acid solubility tests are influenced by solid/solution and P/solution ratios (Braithwaite, 1987 and Braithwaite and Rogers, 1985). To overcome these problems, Lehr and McClellan (1972), proposed the absolute citrate solubility (ACS) using the neutral ammonium citrate extractant. They demonstrated that ACS could be estimated from the unit-cell a dimension of an apatite. Axelrod and Gredinger (1979) confirmed that accessory minerals in PR interfere with the reactivity tests.

Studies on the influence of various potential impurities (calcium chloride, calcium sulfate, monocalcium phosphate, monosodium phosphate, calcium carbonate, sodium carbonate and iron and aluminum sulphates) on the solubility of North Carolina and Youssoufia (Morocco) PR in 2% citric and 2% formic acids by Braithwaite et al. (1989) showed that these impurities affected the extraction of P with 2% formic acid more than with 2% citric acid. They further examined the effect of solid/solution ratio on the P extracted from North Carolina, Nauru-Christmas, Khourigba and Youssoufia PRs and showed that it was more affected by the solid/solution ratio when citric acid rather than formic acid was used. In addition, they pointed out the suppression of P solubility, due to common ion effect, observed after addition of calcium chloride, calcium sulfate and calcium phosphate. The solubility was severely depressed by addition of calcium carbonate and sodium carbonate due to reaction with the acidic extractants.

The reactivity of seven PRs by five laboratory methods, including neutral ammonium citrate, 2% citric acid, 2% formic acid, ammonium citrate pH 3 and absolute citrate solubility was evaluated by Chien and Hammond (1978). They correlated the solubility tests results with the dry matter yield of guineagrass (Panicum maximum) grown under greenhouse conditions. The calculated correlation coefficients showed, at all application rates (50, 100, 200, 400 ppm P), higher correlations for ammonium citrate pH 3 and lower correlations for absolute citrate solubility. Chien and Hammond (1978) concluded that neutral ammonium citrate and ammonium citrate

pH 3 were the best methods for ranking PRs according to their agronomic potential. They criticized the use of the absolute citrate solubility method proposed by Lehr and McClellan (1972), which utilizes x-ray diffraction technique to assess reactivity of a PR in which apatite is intermixed with siliceous minerals. Mackay et al. (1984) compared the ability of seven chemical extractants to estimate the agronomic effectiveness of six PRs by using perennial ryegrass (Lolium perenne) and white clover (Trifolium sp) grown under greenhouse conditions on six soils. The chemical extractants included: 2% formic acid, 2% citric acid (30 min. and 60 min. equilibration time), neutral ammonium citrate, alkaline ammonium citrate, 5% citric acid and 15% citric acid. This study showed that 2% formic acid was the most useful single extraction method. Because PR contains calcite, Mackay et al. (1984) argued that a single extraction procedure may not be suitable and showed the importance of using a multiple extraction procedure to reduce the effect of soluble impurities contained in PRs. Marwaha (1985) developed a fertility index of phosphate rock (FIR = neutral ammonium citrate + loss on ignition/100) for assessing PR for direct application to soils. In this study, he evaluated in a greenhouse experiment the P response of flooded Nato rice to six PRs. He compared the chemical properties of the PRs and the data on dry matter yield and found that the loss on ignition, AOAC citrate solubility, Na_2O, and absolute citrate solubility correlated the best with crop responses. Three models were then developed and an agronomic suitability range was proposed: FIR < 0.24 unsuitable, $0.25 \geq$ FIR ≤ 0.64 moderately suitable, $0.65 \geq$ FIR ≤ 1.04 suitable,

and FIR ≥ 1.05 highly suitable. Before the work by Marwaha (1985), Chien and Hammond (1978) had already grouped seven PRs into three groups of reactivity based on relative agronomic potential (RAP): high, medium and low. Leon et al. (1986), however, recognized an additional group of very low reactive PRs. The investigated samples included those of Hammond (1977) and seven igneous and metamorphic PRs. Previously, Diamond (1978) proposed a threefold classification into low, medium and high based on formic acid, neutral ammonium citrate, and citric acid solubilities. The agronomic effectiveness of a PR is the expression of its chemical reactivity, however. When PR is applied to soil, the availability of P from the rock is influenced by internal and external factors: physical conditions of PR, fertilizer management, soil properties, and crop type (Hammond et al., 1986).

Factors Affecting Phosphate Rock Dissolution

The effectiveness of a PR in releasing plant-available P when added to soil varies significantly. In the following discussion, it will be shown that independently of the source and the form of PR, its dissolution in soil is largely determined by internal and external factors.

Internal factors

The congruent dissolution of apatites requires the release of Ca^{2+}, $PO4^{3-}$, F^{-}, CO_3^{2-}, OH^{-}, Mg^{2+}, and Na^{+} from the apatite surface, with the PO_4^{3-} rapidly converted to $H_2PO_4^{-}$ and HPO_4^{2-} (Khasawneh and Doll, 1978). The gradient in

chemical potential of these ions constitutes the driving force for PR dissolution. Chien and Black (1976) studied the free energy of formation of carbonate apatite and showed that its solubility product varies considerably with the degree of carbonate substitution for phosphate in the apatite structure. They reported the following relationship $pK_{CA} = 122.2 - 6.3X$, where pK_{CA} is the negative logarithm of the solubility product of carbonate apatite (CA) and X is the moles of CO_3^{2-} per mole of apatite. Moreover, Chien and Black (1976) derived the theoretical equation for the standard free energy of formation of carbonate apatite ($\Delta G°_{f,CA} = -3087.9 + 116.1X$). Using the $\Delta G°_{f,CA}$ equation reported by Chien and Black (1976) and the standard free energy of formation of Ca^{2+}, Na^{+}, Mg^{2+}, PO_4^{3-}, CO_3^{2-}, and F^{-} values published by Rossini et al. (1952), Chien (1977) calculated the standard free energy of dissolution of carbonate apatite ($\Delta G°_{d} = 163.3$ Kcal). This relationship showed that the dissolution of carbonate apatite does not depend on carbonate substitution, and the positive sign indicates that a driving force must be provided. Such a driving force is provided by H ions in acid solution. Chien (1977) also calculated the standard free energy of neutralization of anions of apatite with H ions and found that $\Delta G°_{n} = -(165.8 + 5.1\ X)$, where $\Delta G°_{n}$ is the standard free energy of neutralization of anions of apatite. As it can be seen from the negative sign, the neutralization reaction is a spontaneous process. The computed standard free energy of reaction of a carbonate apatite in acid medium ($\Delta G°_{R}$) as the sum of $\Delta G°_{d}$ and $\Delta G°_{n}$ values showed that $\Delta G°_{R} = -(2.5 + 5.1\ X)$.

This states that the negative free energy increases with increasing carbonate substitution.

External factors

Although it has been recognized that agronomic effectiveness of PR is expressed by the degree of carbonate substitutions for phosphate in the apatite structure, external factors such as physical conditions of PR and soil properties strongly influence the agronomic effectiveness of a PR.

a. Physical factors. In general, the solubility of PR is very low, and when applied to soil, the P concentration increases only in the close vicinity of the PR particles. Thus, the degree of contact between the PR particles and the soils particles will dictate the P release into soil (Khasawneh and Doll, 1978). Reviews by Khasawneh and Doll (1978) and Cooke (1956) provided evidence that grinding PR to fine particles improved PR dissolution. They pointed out, however, that grinding finer than 100 mesh does not increase dissolution of PR under laboratory or greenhouse conditions.

b. Soil factors. Soil pH, exchangeable Ca, and P retention capacity are the key factors that determine the P release into soil. Numerous research reports, including those of Peaslee et al. (1962) and Ensminger et al. (1967), provided evidence that the P release is greater in acid soils than in neutral or alkaline soils. At low pH, francolite is very unstable and releases P to the soil solution that reacts with Al and Fe to form more stable compounds than apatites (Khasaw-

neh and Doll, 1978). Kanabo and Gilkes (1987a), using a single soil modified to various pHs, observed that PR dissolution increased linearly with decreasing pH. Similar trends were found by Kanabo and Gilkes (1987b) when they incubated North Carolina PR in a lacteritic podzolic soil adjusted to different pH values by adding dilute HCl or solid $SrCO_3$. Their results showed a large increase in bicarbonate-soluble P with increasing acidity; the extracted bicarbonate-soluble P was 100% greater at pH 4.55 than at pH 5.78. The soil incubation data were correlated with dry matter yield of clover grown under greenhouse conditions on soils that received no P and 800 mg P kg^{-1} soil as North Carolina PR. The relationship between soil pH and clover dry matter yield indicated no influence due to change in pH. They suggested that the absence of response maybe attributed to the high level of P applied. The investigators, however, reported an increase in P content of plants relative to the control plants for all pH levels. Liming acid soils as a general rule, decreases the effectiveness of P release from PR.

Dissolution of PR in soil is promoted by soil's affinity for Ca. Soil provides a sink for Ca that is released by dissolution of PR and for every 10 moles of Ca dissolved, 6 moles of P is released into solution (Khasawneh and Doll, 1978). When PR is applied to a soil with low Ca affinity, Ca concentration increases at the apatite surface and consequently the level of orthophosphate ($H_2PO_4^-$ or HPO_4^{2-}) decreases. In an investigation of the effect of Ca gradients on PR dissolution in systems of H-

humus, H-amberlite and H-Putman clay, Graham (1955) found that weathering of P from PR was related to active Ca and active H ions in the hydrogen-saturated colloidal systems.

Phosphate rock dissolution increases with increasing P retention capacity, whereas the amount of plant-available P in soil declines (Hammond et al., 1986). Studying 16 different acid soils from Colombia treated with North Carolina PR, Chien et al. (1980) observed that the water-extractable P in soils declined as P retention capacity increased. Experiments conducted by Harris et al. (1984) in the Philippines and Indonesia also confirmed the finding that effectiveness of PR is reduced by high P retention capacity in soils.

Calcination may increase total P content of PR. Investigation by Chien and Hammond (1991) on the effect of calcination on agronomic effectiveness of PR showed a decrease in carbonate for phosphate substitution in North Carolina apatite structure from 1.20 to 0.32 moles. Moreover, a solubility test in neutral ammonium citrate showed a decrease in P release from 2.7 to 0.8%. In addition, the dry matter yield and uptake by corn (Zea mays L.) grown on Hartsells silt loan soil showed a decline as a result of calcination.

Alternative Ways for Increasing P Availability from Phosphate Rock

Throughout this review, it was shown that not all PRs are agronomically effective. The vast majority of PR deposits found in the world are classified as low reactive PRs and cannot, therefore, be successfully used as P sources for crops. The

traditional way used to increase the solubility of PR is the acidulation of PR with sulfuric acid to produce single superphosphate (SSP) or with phosphoric acid to produce triple superphosphate (TSP). However, the cost of production of these phosphate fertilizers is continuously increasing and it is, therefore, necessary to seek other alternatives to increase P availability in PRs.

Alternative ways to increase P availability from PR include: (1) incorporation of additives into PR, (2) partial acidulation of PR, (3) compaction of PR with water-soluble P fertilizers, and (4) microbiological methods. These are discussed below.

Incorporation of additives

Several studies have been reported on the effects of addition of various N sources and elemental S on PR dissolution. Greenhouse studies by Volk (1944) on the effect of urea or ammonium sulfate mixed with Tennessee PR on oat (Quercus sp) and sorghum (Sorghum vulgare) yields showed that these compounds increased dry matter yields. However, the yields from the mixed fertilizers were lower than those obtained from ordinary superphosphate. Terman et al. (1969) studied PR granulation with acidic materials and found that PR granulated with urea or ammonium nitrate did not increase the P availability, whereas granulation of PR with urea nitrate or with oxalic acid increased the P availability. In all cases, P availability from concentrated superphosphate was better than from any of the acidic materials tested. Even though studies by Jones (1948) suggested that $(NH_4)_2SO_4$ and KCl increased the availability of P in PR to plants, it is not well known whether the increase in availability of P is chemical or

biological through plant root growth stimulation. Chien (1979) investigated the dissolution of North Carolina PR mixed with increasing amounts of $(NH_4)_2SO_4$, urea, or KCl in two acid soils. He reported that the dissolution of the PR was depressed by KCl and $(NH_4)_2SO_4$ addition, whereas addition of urea increased the dissolution. He concluded that the decrease in PR dissolution in the presence of KCl or $(NH_4)_2SO_4$ was due to an increase in P sorption capacity of the soils. On the other hand, the increase in water-soluble P observed by addition of urea was the result of high pH that led to hydrolysis of the soil organic matter; products of this hydrolysis chelated the Ca ions associated with phosphate. The beneficial effect of mixing PR with elemental S has been practiced with the logic that Thiobacillus sp. would oxidize S to H_2SO_4, which would then react with PR to release P (Khasawneh and Doll, 1978). Neller (1956) investigated the effect of sulfur and gypsum additions on P availability from PR in a Leon fine sandy soil. He reported a significant effect of S on P availability to oats and clover. Measurement of soil pH taken three months after S addition showed a reduction in soil pH. Maximum growth was obtained at S application rate of 800 lb $acre^{-1}$; soil pH at this S application rate was 6.54. At S application rate of 1600 lb $acre^{-1}$, plant growth was retarded and the reported soil pH was 5. Neller and Bartlett (1959) studied the effect of S addition on P availability from PR to forage crops on a Leon fine sandy soil. They observed an increase in yields and P content. However, the increase was not significant at 5% level. Radioactive measurement of residual P availability did not show any increase in P availability as a result of S addition.

Several researchers reported an increase in P release after composting PR and S (Lipman et al., 1916; Lipman and Mclean, 1918). Lipman et al. (1921), as cited by Khasawneh and Doll (1978, p. 182), demonstrated the importance of thiobacillus in PR solubilization in presence of S. In a field experiment, they observed high yields when barley (Hordeum vulgare L.) seed was inoculated with Thiobacillus before planting on a plot that received PR + S. Basak and Debnath (1987) reported an increase in grain yield, Olsen extractable P of the rhizosphere soil, and P uptake by bread wheat cv. sonalika (Triticum aestivum Linn. emend. Friori and Paol) when Mussoorie PR was composted with decomposing rice straw and fresh cow manure. No favorable effect was observed, however, from composting a Purulia PR and basic slag from Tata Steel Mill (100 mesh) in terms of grain yield and Olsen extractable P.

Partial acidulation

Another approach to make P more readily available to plants is partial acidulation. Partial acidulation means that only a proportion of the acid required to produce the conventional fertilizer (fully acidulated) is used. For example, Partial Acidulated PR (PAPR) 50% H_2SO_4 refers to the use of 50% of sulfuric acid required to produce SSP; PAPR 20% H_3PO_4 refers to the use of 20% of phosphoric acid required to produce TSP. Following are the main advantages of PAPR as summarized by Hammond et al. (1986): (1) PAPR contains both P in a readily available form to plant and P available over a long term, (2) when the PR is treated with phosphoric acid, it increases the P concentration in the PAPR product, (3) when the PR is treated with

sulfuric acid, the new product contains S for plant nutrition, (4) the quantity of acid needed is decreased, (5) the manufacturers production capacity is increased, and (6) PRs that have a low reactivity or that cannot be used in superphosphate production can be utilized.

The International Fertilizer Development Center (IFDC) has initiated several laboratory and greenhouse experiments to evaluate PAPR products. Hammond et al. (1986) studied the influence of the chemical characteristics of four PRs from Media Luma (citrate solubility: 2.3%), Huila (citrate solubility: 3.5%), Bayover (citrate solubility: 5.3%), Hahotoe (citrate solubility: 3.0%) on dry matter yield of corn grown on two different soils (Mountview and Hartsell soils). They found a good correlation (r=0.92) between P uptake and water-soluble P from the PAPR 50% H_2SO_4 and concluded that the corn responded to the water-soluble P rather than to the citrate-soluble P.

Mokuwunye and Chien (1980) investigated the effect of P fixing capacity of soils on the relative water solubility of North Carolina PAPR 20% H_3PO_4 and Triple Superphosphate (TSP) in three soils (two from Nigeria and one from Colombia). They reported that soils treated with PAPR-20% H_3PO_4 showed relative increases in soil solution P concentration (compared to that of TSP) as the P fixing capacity increased. In another study, Chien and Hammond (1988) also found that the relative agronomic effectiveness (RAE) of Pesca PAPR-50% H_2SO_4 increased from 84% to 124% when the P-fixing capacity increased from 5.6% to 56.1%. Chien and Hammond (1988)

explained the better performance of PAPR compared to TSP or SSP in soils with high P fixing capacity by the chemistry of soil reactions. The hydrolysis of monocalcium phosphate in PAPR, TSP, and SSP resulted in formation of phosphoric acid that dissolved (in case of TSP/SSP) Fe and Al minerals, which reacted with water-soluble P to form water-insoluble Fe and Al phosphates. Consequently, the amount of available P from TSP and SSP decreased as a result of the phosphate fixing process. In the case of PAPR, the H_3PO_4 formed was neutralized by the unacidulated PR of PAPR and additional water-soluble P was released into the soil solution. In low P fixing capacity soils, better performance of crops with PAPR with respect to TSP/SSP was due to an early plant root development that was encouraged by the water-soluble P component of PAPR. This "starter effect" was demonstrated by IFDC in a greenhouse experiment (Chien and Hammond, 1988).

It has been pointed out that PAPR and TSP are less influenced by soil pH and liming than PR (Chien and Hammond 1988). IFDC also conducted field evaluation of PAPR in Latin America, Asia, and Sub-Saharan Africa. Three experiments were carried out in Togo (Alfisol), Nigeria (Alfisol) and Sierra Leone (Ultisol) to compare RAE of Togo PR, Togo PAPRs (with sulfuric acid at 25 and 50%) to SSP. The RAE expressed by maize grain yield was 72% in Nigeria, 82% in Togo, and 103% in Sierra Leone. On an oxisol at Sapu (dry region of The Gambia) Tilemsi (Mali) PR and Tilemsi PAPR were equally effective as SSP in groundnut (Arachis hypoea) and corn production. Studies in Burkina Faso and in Niger on Alfisols using Kodjari PAPR-

50% H_2SO_4 and Parc W PAPR-40% H_2SO_4 PAPRs were, respectively, 75% and almost 100% as effective as SSP (Bationo et al., 1986). Bationo et al. (1990) evaluated the agronomic effectiveness of Tahoua and Parc W acidulated with H_2SO_4 at 50% (50% H_2SO_4) in sandy soil in Niger and concluded that partial acidulation of Tahoua PR with sulfuric acid was not appropriate. The rock contains high Fe_20_3 plus Al_20_3 that reduced water-soluble P in the PAPR material. Hammond et al. (1989) reported that PR containing high amounts of Fe and Al considerably reduced water-soluble P and agronomic effectiveness of the derived PAPR product. They found that PAPR-50% H_2SO_4 made from Kodjari PR (7.1% Fe_2O_3 + Al_2O_3) was only 49% as effective as TSP in dry matter production, whereas PAPR-50% H_2SO_4 made from Hahotoe PR (1.9% Fe_2O_3 + Al_22O_3) was 84% as good as TSP. The same conclusion was reached by Menon et al. (1991) when they compared the effectiveness of PAPR-50% H_2SO_4 and compacted TSP with PR from Capinota (low reactive PR containing 8.8% Al_2O_3 + Fe_2O_3) or with PR from Huila (medium reactive PR, containing 2.3% Al_2O_3 plus Fe_2O_3) by using upland rice and Kidney bean (Phaseolus vulgaris) as test crops. Compaction of Capinota PR with TSP increased the effectiveness of the rock from 43% before compaction to 80% after compaction for rice grain yield and from 51% before compaction to 92% after compaction for kidney bean dry matter yield.

Compaction of PR with water-soluble P fertilizers

While partial acidulation is a way to improve agronomic effectiveness of low reactive P rocks, compaction with TSP/SSP is an alternative approach to improve agronomic effectiveness of PRs high in Fe_2O_3 and Al_2O_3 contents (Chien and Hammond, 1988). The positive effect of addition of TSP to PR has been reported in the literature. TSP in combination with PR enhances P uptake, increases top and root growth, promotes solubility and availability of soil P. Chien et al. (1987a) studied the combination effects of TSP and a reactive PR from North Carolina on yield and P uptake by corn grown on a limed soil (pH 6.2) and observed an increase in dry matter production and P uptake as the proportion of TSP to PR in the mixture increased. They pointed out that even though the North Carolina rock by itself was less effective than TSP, its combination with TSP at a 1:1 ratio was as effective as TSP.

Phosphorus availability from compacted rocks with urea or with urea and TSP was investigated by Chien et al. (1987b). They compared the agronomic effectiveness of Pesca PAPR-20% H_3PO_4 with that of compacted (PR + TSP) and compacted (PR + TSP + urea) and found that the effectiveness of PAPR-20% H_3PO_4 and compacted (PR + TSP) were equal; the compacted (PR + TSP + urea) was 30% more effectiveness than compacted (PR + TSP). The authors concluded that urea hydrolysis increased the P availability from PR.

On an acid Bladen sandy loam soil (typic Albquilt), Kpomblekou et al. (1991) evaluated the relative agronomic effectiveness (RAE) of four phosphate fertilizers

(ground Togo PR, partially acidulated phosphate rock, (PAPR-50% H_2SO_4), Togo PR compacted with TSP or SSP using corn and cowpea (Vigna sinensis) as test crops. The calculated RAE values with respect to SSP was 72.5% for PAPR-50% H_2SO_4 and 84.7% for compacted PR + TSP in corn dry matter production and 87.7% and 97.1%, respectively, in cowpea seed yield.

Only a limited amount of literature exists on chemical ways to increase P availability of PR; on the other hand, biological means to increase available P of PR are very limited. The most frequent biological means used include the use of solubilizing bacteria and mycorrhizal fungi. Kucey and Leggett (1989) conducted field and greenhouse experiments to study yields and P uptake by Westar canola (Brassica napus L.) inoculated with a phosphate-solubilizing isolate of Penicillium bilaji on a brown chernozemic soil. The four fertilizer treatments used included: 20 mg P kg^{-1} soil of Florida PR (ground to < 150 μm), 10 mg P kg^{-1} soil of monoammonium phosphate (MAP), 20 mg P kg^{-1} soil of MAP, and a control without fertilizer. Their results suggested an increase in P uptake by inoculated Canola. The P uptake from Florida PR treatment plus inoculation was close to the P uptake from MAP without inoculation. Moreover, the P uptake by inoculated control plants was as high as the P uptake from inoculated canola that received MAP. Earlier, Asea et al. (1988) examined the solubilizing effect of Penicillium bilaji and Penicillium fuscum on Idaho PR ground to 63 mesh in liquid culture and found that the extent of inorganic P solubilization was directly related to the decrease in pH caused by each isolate. They also reported an

increase in P uptake (14%) and in dry matter yield (16%) of inoculated (P. bilaji) wheat grown on calcareous chernozemic soil treated with Idaho PR. Kucey (1987) observed that addition of Idaho PR (45 mg P/kg soil) to a calcareous soil inoculated with P. bilaji produced dry matter yield and P uptake that were not significantly different from yield and P uptake of wheat and beans that received 15 mg P kg^{-1} soil as TSP. The increase in uptake of soil immobile nutrients, mainly P, has been viewed as the primary beneficial role of mycorrhizae on plant growth. It is generally agreed that mycorrhizae increases P uptake from poorly soluble P fertilizers more than from soluble P fertilizers. Pairunan et al. (1980) pointed out that mycorrhizal plants were better than non-mycorrhizal plants in solubilizing P from PRs, but pointed out that the increase in uptake from PR was the same as from the soluble-P fertilizers. Bolan et al. (1987) compared three phosphate compounds of various solubility: KH_2PO_4, crystalline FE phosphate, and colloidal iron phosphate as P source. Mycorrhizal and non-mycorrhizal subterranean clover and ryegrass were grown. The largest increase in P uptake was obtained with the least soluble iron phosphate source. Two main factors favor plants having mycorrhizae: (1) increased hyphae surface area that allow the plant to explore more soil (Richards, 1974; Harley, 1975) and (2) produced exudates by the fungi may mobilize a great amount of soil nutrients (Bowen, 1973; Harley, 1975). Malajczuk and Cromack (1982), identified a dense concentration of calcium oxalate crystals in the mantle of ectomycorrhizae of Pinus Radiata and Eucalyptus Marginata and suggested that oxalate production by the fungi may increase nutrient

uptake by root tissue. Cromack et al. (1979) reported 20 times more accumulation of calcium oxalate in fungal mats of ectomycorrhizal basidiomycetes than in uncolonized soil. Production of oxalic acid is common to many fungi and soil weathering processes have long been associated with production of organic acids; release of these acids increases P, Ca, Mg, Fe and Al availability to plants (Fisher, 1972).

Production of Low-Molecular-Weight Organic Acids in Soils

Low-molecular-weight (LMW) organic acids are commonly present in most agricultural soils. These acids are produced in soil as microbial metabolites or plant exudates from dead or living cells. Concentrations of LMW organic acids in soils are very low (10^{-3} to 10^{-5} M); however, under suitable environmental conditions, these acids may accumulate to levels toxic to plant growth. The most common LMW organic acids identified in soils are oxalic, succinic, tartaric, fumaric, malic, citric, sinapic, caffeic, syringic, salicylic, gallic, p-coumaric, gentisic, protocatechuic, vanillic, p-hydroxybenzoic, and ferulic (Kaurichev et al., 1963, Stevenson, 1967). Contrary to long-chain fatty acids that may persist in soils for long periods of time, LMW organic acids have transitory existence; the amount present in soil at any time, is a balance between synthesis and destruction processes controlled by microorganisms. Stevenson (1967) found that LMW organic acids reach their highest equilibrium level during active plant residue decomposition.

Sources of organic acids in soils may vary significantly. In a forest ecosystem, natural depositions of leaves, organic debris, organic substances from root and

branches decomposition represent valuable sources of soluble organic substances. Pohlman and McColl (1988) identified five aliphatic acids (oxalic, maleic, aconitic, malic, and fumaric) and six aromatic acids (gallic, protocatechuic, p-hydroxybenzoic, vanillic, benzoic, and p-coumaric) in O, and O_2 litter of seven overstory and understory forest species. The amount and kind of organic acid present in forest litter vary with tree species and period of the year. Although oxalic and succinic acids are present in most tree species, only small amounts of oxalic and tartaric acids were found in the pine rhizosphere (Spakhov and Spakhova, 1970). The amounts of the acids in soils tend to decrease during the middle of the growing season, but as fall approaches the amounts increase to reach high levels. This pattern in concentrations of organic acids seems to correspond to the seasonal rhythm of root secretion (Spakhov and Spakhova, 1970).

Among the organic substances identified in the rhizosphere, organic acids are the most abundant component. In the root exudates of barley and wheat, Vančura (1964) identified two keto-acids (pyruvic and oxalacetic acids) and various di- and tricarboxylic acids (uronic, oxalic, malic, glycolic, succinic, and fumaric acid). Besides low-molecular-weight (LMW) compounds found in the rhizosphere, high-molecular-weight (HMW) gelatinous materials and sloughed-off cells and tissues and their lysates have been reported (Marschner, 1986). Phenolic compounds, amino acids, aliphatic acids and various sugars are the main components of the LMW fraction of root exudates. Rovira and Davey (1974) reported the presence of enzymes, amino acids, aliphatic

acids, flavimones, nucleotides, and various sugars in root exudates of wheat (Triticum aestivum L.). Describing the significance of forest tree root exudates, Smith (1976) collected and analyzed root exudates from unsuberized tips of new woody roots from three mature trees (Betula alleghaniensis, Fagus grandifolia and Acer Saccharum) and found various amounts of acetic, citric, aconitic, oxalic, fumaric, and malic acids. The kind and the amounts of organic acids found varied with the tree species.

Anaerobic conditions are favorable to microbial synthesis of organic acids. Takijima (1960, as cited by Stevenson, 1967, p. 129) detected 13 organic acids in paddy soils; the acids accumulated in order of acetic > butyric > formic > fumaric, propionic, valeric, succinic and lactic. Large amounts of aliphatic organic acids have been found also during organic matter fermentation in submerged soils. During incubation of wheat straw under anaerobic conditions, Wallace and Elliott (1979) identified acetic, butyric, and propionic acids in the straw extract. Rao and Mikkelsen (1977) identified acetic acid as primary organic acid produced during incubation of rice straw with flooded soil. Mitsui et al. (1959) found that organic acids accumulated at low temperatures rather than at high temperatures due to a slow decomposition of the acids at low temperatures. It is recognized that organic acids tend to accumulate in poorly drained paddy soils; the greatest accumulation was found under the lowest (most negative) redox potential values.

Many researchers have shown that crop residues suppress plant growth. Boerner (1956) detected vanillic, p-hydroxybenzoic, p-coumaric, and ferulic acids in crop

residues and showed, through water culture, that p-hydroxybenzoic and p-coumaric depressed rye (Secale cereale L.) and wheat root elongation, whereas these two acids encouraged barley root elongation. Although phytotoxic effects of organic acids have been reported, organic acids present in soils play an important role in solubilization, mobilization and transport of mineral matter.

Complexing and Chelation of Metals by Organic Acids

Biochemicals that have the ability to chelate metal ions are produced in soils through microbial activities. Even though these biochemicals, naturally produced in soil have a transitory existence, significant amounts may be detected in the soil solution during periods of intense microbial activity. Organic materials and their organic acids are capable of complexing or chelating metals by ion-exchange, surface adsorption, coagulation and peptization reactions (Mortensen, 1963). By forming soluble complexes with polyvalent cations from rocks and minerals, organic acids play an important role in dissolution, transportation, and concentration of elements in the earth's surface (Huang and Kiang, 1972) as well as in soil formation and plant nutrition.

Several organic acids identified in soil exhibit metal chelation properties. Di- and tri-carboxylic acids that contain β-hydroxyl functional groups, and phenolic acids with OH groups at the ortho position dissolve Fe, Al, and Mn from soil faster than other similar organic compounds possessing different functional group combinations (Pohlman and McColl, 1986). Structures of ligands and relative stabilities of the complexes formed vis à vis E_h and pH are the key factors that determine whether the

complexes formed are soluble or insoluble (Huang and Keller, 1972). Affinity of a metal for a specific organic acid determines the stability of the metal chelate complex; this stability generally increases with increasing charge of the metal ion and the number of rings formed by a molecule of chelant (Lehman, 1963). Lehman (1963) examined the stability constants for Ca and showed that five-membered ring chelates are the most stable. Several workers have demonstrated the effectiveness of various organic acids in mineral weathering. Boyle et al. (1974) studied biotite weathering by six organic acids (oxalic, malonic, citric, lactic, malic, and propionic) of a wide range acid strengths, chelating abilities, and molecular structures. Results showed that organic acids extracted more Fe, Al, or Mg than HCl of about the same pH and suggest that weathering of biotite was accelerated by the chelation ability of the organic acids. Oxalic acid and citric acid are effective in releasing K from potassium-bearing minerals. The effectiveness of these acids, however, depends on the chemical composition, atomic bonding, crystal structure and formation sequence of K-bearing minerals (Song and Huang, 1988). Song and Huang (1988) examined the dynamics of K release from mica and K-feldspars in the presence of oxalic and citric acids and found that the release from biotite was 14 to 18 times faster than from K-feldspars. Dissociation of H^+ ions from organic acids causes dissolution of minerals by lowering the pH of the solution. Dissolution of feldspars by low-molecular-weight aliphatic and aromatic acids showed a good correlation between total amounts of elements and Al released and solution pH (Manley and Evans, 1986). Thus, Manley and Evans (1986) concluded

that the strength of the acid was more important in solubilization of elements than the ability of the acid to complex metal cations. A previous work, however, classified organic solvents in order of increasing effect of dissolution as acetic, aspartic, salicylic, and citric acids (Huang and Kiang, 1972). This order corresponds with the complexing order of these acids.

There are two main mechanisms that may occur successively in alteration of minerals in presence of organic acids: (i) organic acids dissociation with proton release; this is a rapid process, precursor of structural destruction of mineral and release of elements into solution and (ii) complexing reactions (much slower) that occur between ligands and certain elements (Fe, Al) already in solution (Razzaghe and Robert, 1979). Aqueous extracts of leaves of some tree species are capable of mobilizing Fe. This was demonstrated by Muir et al. (1964) when they used dried pine needles containing malic and citric acids to solubilize (Fe from Fe-bearing minerals) and maintain Fe in solution from pH 4 to pH 9.5. Huang and Keller (1972) studied the weathering of silicate minerals in presence of weakly complexing acids (acetic and aspartic) and strongly complexing acids (citric, tartaric, salicylic, and tannic). Their work showed that the weakly complexing acids dissolved up to 10 times more Al and Fe than water; the strongly complexing on the other hand, dissolved Al and Fe up to 1,000 times more than water due to the formation of stable water-soluble Al or Fe organic complexes or chelates in the solution.

The role of organic acids in soil genesis is well known. Formation of the spodic horizon of spodosols has been associated with production of organic acids, formation of

stable fulvic acid-Al^{3+} (or Fe^{3+}) chelate, translocation and precipitation of metals. During the initial stage of biological breakdown of fresh organic materials, organic acids such as citric, oxalic, acetic, fulvic and humic acids are produced in the O or A soil horizon. These acids have large amounts of COOH, and phenol OH radicals that bind Al^{3+} and Fe^{3+} to form stable organo-metallic complexes that migrate with percolating water from an O or A horizon to a B horizon where precipitation occurs (Bruckert, 1970). Bruckert (1970) showed that only aliphatic acids play a major role in the complex formation and transport of Fe and Al. Organic acids also influence the release of P and Al from spodic horizons and may be an important factor in plant nutrition. For 16 organic acids studied, the release of Al and inorganic P increased exponentially with increasing stability constants except for salicylic acid (Fox et al., 1990).

Effect of Organic Acids on P Release from P-bearing Minerals

Several isolates obtained from the rhizosphere of various plants grown in culture media have shown the ability to solubilize phosphate minerals. The organic-acid fraction of these isolates has been shown by several researchers (Sperber, 1957; Louw and Webley, 1959) to be primarily responsible for the solubilizing effects. Soluble rhizosphere products derived from wheat, pea (Pisum sativum) and corn were effective in dissolving synthetic hydroxyapatite; the degree of solubilization, however, differs with plant species in the order of wheat > corn > pea (Moghmi et al., 1978). The active components of the rhizosphere products of wheat seedlings were shown to be in

the u.v. absorbing fraction and in the acidic fraction. A large number of organic acids including aliphatic and aromatic acids have been tested for their ability to dissolve dicalcium and tricalcium phosphate; reactions involved in the dissolution process are not only pH dependent but are also related to the structural characteristic of the acid (Johnston, 1952, 1954a). Among the acids used by Johnston (1954a), α-hydroxy aliphatic acids were more effective than other aliphatic acids with β-substitution in dissolving tricalcium phosphate. Studies including several aromatic organic acids also confirmed that action of these acids on tricalcium phosphate depends on their structure. Johnston (1954b) showed that as the hydroxyl group is removed further from carboxyl group of the benzoic acid, the power of the acid to remove phosphate from tricalcium phosphate is reduced. Substitution of an amino group into benzoic acid diminishes the power of the acid to dissolve the phosphate and decreases its dissociation constant. Organic acids are also very effective in dissolving phosphate from Fe and Al phosphates; citric acid, a tri-carboxylic acid is more powerful than HCl or any other organic acid in solubilizing Al or Fe-phosphates (Johnston, 1959). Moghimi and Tate (1978) studied the dissolution of synthetic hydroxyapatite in presence of α-ketogluconitic acid, citric acid, acetic acid, and EDTA and found that the effectiveness for dissolution of hydroxyapatite increased in the order of α-ketogluconate $\leq$ acetate $\leq$ citrate $\leq$ EDTA. The measured stability constant for 2-ketogluconate suggested that 2-ketogluconitic acid is not an effective chelating agent for Ca. When soluble P fertilizers are added to acid soils, some specific compounds of taranakite, strengite-

barrandite-variscite series are formed. These compounds are very insoluble, and have the greatest stability at low pH (pH 3.0 for Fe salt and pH 4.0 for Al salt). Citric, tartaric, oxalic, malic, malonic, and lactic acids were found to form metal-organic complex molecules of great stability with Fe and Al and so prevent precipitation of phosphate (Bradley and Sieling, 1953). Chaudhary and Mishra (1980) studied the effect of complexants on the transformation of Mussoorie PR in an acid soils system. Their results showed the superiority of citric over oxalic and EDTA in increasing dissolution of the rock. They concluded that the better performance of citric acid may be due to a formation of more stable complexes with Ca. Effectiveness of PR may also be increased by addition of organic substances such as sucrose, glucose, and pectin; starch on the other hand decreased the effectiveness of the rock (Dalton et al., 1952). Effective chelation between Ca and organic anions will result in great release of P from PR. Johnston (1956) showed that structure of organic acids play an important role in the stability of the complex formed and that Ca chelates weakly with α-hydroxy aliphatic monobasic acids, strongly with dibasic and most strongly with tribasic aliphatic acids.

Although information is available on alternative ways to increase P availability in PR with various acidic additives, there is only limited information on the use of organic acids to enhance P availability in PRs. Therefore, information is needed on the effect of various aliphatic and aromatic acids on P release in PR. This is important because the naturally occurring organic acids can complex polyvalent metals and release P into soil solution to increase plant-available P.

PART I. REACTIVITY AND TRACE METAL CONTENTS OF PHOSPHATE ROCKS FROM VARIOUS DEPOSITS

INTRODUCTION

There has been a growing interest in the use of phosphate rock for direct application. Therefore, a laboratory reactivity index has been developed for comparing the agronomic potential of various phosphate rocks (PRs). Although field tests are the most reliable for assessing agronomic effectiveness of PRs, these tests are costly and time consuming. To overcome these problems, x-ray diffraction techniques and laboratory solubility tests have been used to determine PR reactivity. Even though determination of the reactivity of PR by x-ray diffraction methods represents the most appropriate means, its routine use has been limited by high cost equipment and materials that are not available in many laboratories. Consequently, alternative chemical reactivity tests are widely used. These chemical reactivity tests are solubility tests performed with various chemical extractants to estimate the agronomic potential of PR. Four extractants are mainly used to evaluate reactivity of a PR: neutral ammonium citrate (pH 7, first and second extractions), ammonium citrate pH 3, 2% citric acid and 2% formic acid. There is no standardized method for determining reactivity of PR; however, the International Fertilizer Development Center (IFDC) tends to favor the use of the second extraction by neutral ammonium citrate to evaluate the reactivity of PRs. Conclusions reached by solubility tests in predicting agronomic effectiveness of PR vary considerably. Chien and Hammond (1978a) found that neutral ammonium citrate (second extraction), 2% formic acid, and ammonium citrate pH 3 solubility tests correlated the best with agronomic data, whereas Caro and Hill (1956) found that 2%

citric acid was a better indicator of agronomic effectiveness. Other studies have shown that 2% citric acid (Cooke, 1956) and neutral ammonium citrate (Bennett et al., 1957) were poor indicators of agronomic effectiveness. Single extraction procedures with the exception of 2% formic acid appear not to be suitable for assessing agronomic potential of PR containing large amounts of $CaCO_3$ (Mackay et al., 1984). Mackay et al. (1984), therefore, recommended a sequential extraction technique.

There is a growing demand by the phosphate fertilizer industry to produce phosphoric acid, single superphosphate, triple superphosphate, and ammonium phosphate. Most western countries (with the exception of the former U.S.S.R., USA, Finland, and Sweden) do not have PR deposits and are completely dependent on imported PRs to support their growing phosphate fertilizer industry. In 1983, developing countries exported nearly 67% of the total PR produced in the world (FAO, 1984). The exported PRs contain, in addition to P, many trace and nontrace metals. Although the concentration of these metals may vary considerably from one deposit to another, many soils receiving P (as PRs or commercial P fertilizers) have been found to accumulate trace metals exceeding the natural abundance of these metals in soils and constitute one of the main sources of contamination of agricultural lands. Because trace metal contents of PR have not been evaluated and because considerable evidence has been shown that heavy metals can enter the human food chain, it is wise to assess trace metal contents of PRs from various deposits. Therefore, the objectives of this

study were: (1) to chemically characterize 12 PR samples obtained from various deposits, (2) to establish the empirical formula of each rock, and (3) to assess trace and nontrace metal contents of the PRs.

MATERIALS AND METHODS

Phosphate Rocks

Twelve phosphate rocks (PRs) of a wide range of reactivity were used. These samples were kindly supplied by the International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama. The PR samples involved were (country in parentheses): Kodjari PR (Burkina Faso), Tahoua PR (Niger), North Carolina PR (USA), Gafsa PR (Tunisia), Khourigba PR (Morocco), Tilemsi Valley PR (Mali), Sechura PR (Peru), Minjingu PR (Tanzania), North Florida PR (USA), Hahotoe PR (Togo), and Parc W PR (Niger) (Table 1). All the experiments were carried out on samples ground to < 100 mesh (150 μm), with the exception of samples used in the x-ray diffraction technique, which were ground to pass 200 mesh (75 μm). Selective properties of the PR studied are compiled in Table 2. All results reported are averages of duplicate determinations and are expressed on a moisture-free basis, moisture being determined from loss in weight after drying at 105° for 36 h.

Procedures

Differences in agronomic effectiveness observed among PRs are largely due to chemical, crystallographic, and mineralogic composition of their apatites. Assessment of the apatite composition of a PR is, therefore, a measure of its reactivity. Procedures used for measuring the reactivity of a PR include: x-ray diffraction method, infrared procedures, specific surface, elemental analysis, and chemical extractants.

Table 1. Origin of the phosphate rocks studied

Country	Deposit
PERU	Sechura
TANZANIA	Minjingu
TUNISIA	Gafsa
USA	North Carolina
MALI	Tilemsi Valley
MOROCCO	Khourigba
USA	Central Florida
USA	North Florida
BURKINA FASO	Kodjari
NIGER	Parc W
NIGER	Tahoua
TOGO	Hahotoe

In this study, the x-ray diffraction method and the chemical extractants were used.

a. X-ray characterization. Representative samples (about 20 g) of the 12 PRs were obtained by repeated riffling on an open pan riffle sampler (model 224A, 32-chute). Each PR sample was finely ground for 7 min to pass a 200-Tyler-mesh in a laboratory disk mill (Siebtechnik, model TE 250) after addition of 10 mL of freon 113 (trichlorotrifluoroethane) to keep the sample moist. The wet powder was transferred to a watch glass and dried at 105°C in a horizontal air flow oven (blue M Electric

Table 2. Selected properties of the phosphate rocks studied

Phosphate rock	pH[a]	Total P	Water-soluble P[b]	Citric acid-soluble P[c]	$CaCO_3$ equiv.[b]
		%	-------mg kg^{-1} PR-------		%
Kodjari	6.0	10.9	41.0	488	1.47
Tahoua	6.5	11.9	0.70	175	1.13
North Carolina	7.2	12.8	0.60	26	8.60
Gafsa	7.5	13.4	0.10	0	10.30
Khourigba	8.1	13.9	0	0	4.52
Tilemsi Valley	7.7	14.0	0.20	0	3.03
Central Florida	7.5	14.3	1.70	323	4.73
Sechura	7.8	14.5	0	0	6.65
Minjingu	9.0	15.0	9.10	0	7.10
North Florida	6.9	15.3	4.80	298	4.43
Hahotoe	6.5	16.1	12.1	469	1.78
Parc W	7.0	17.6	36.1	475	1.37

[a]Phosphate rock:water ratio, 1:2.5.

[b]One gram of phosphate rock was equilibrated with 25 mL of deionized water at 25°C for 24 hours. The mixture was filtered (0.45 μm membrane filter) and an aliquot was analyzed for phosphate by the method of Murphy and Riley (1962).

[c]One gram of phosphate rock was equilibrated with 25 mL of 1mM citric acid at 25°C for 24 hours. The mixture was filtered (0.45 μm membrane filter) and an aliquot was analyzed for phosphate by the method of Murphy and Riley (1962).

[d]By the method of Bundy and Bremner (1972).

Company, model OV-490 A-2) for 2 h. The dried sample was then thoroughly mixed and 1.5 g was weighed out into an agate mortar containing 0.1 g of tungsten (internal standard). The contents of the mortar were thoroughly mixed and a powder mount was made. A special cavity was used by placing a glass slide over the mount and the sample was side loaded into the cavity. The mount was tapped on a counter to compact the sample; the glass slide was removed and the mount was placed in the specimen holder of the Siemens D500 x-ray unit. The flat surface created by the glass slide was used as the x-ray surface. The instrument setting and the method for determining unit-cell parameters of apatites has been described in detail by McClellan and Lehr (1969). The x-ray characterization of the PR samples described above was done by the author at the IFDC laboratories in August of 1991.

b. Neutral ammonium citrate extraction. A 1-g PR sample was equilibrated with 100 mL of neutral ammonium citrate for 1 hour at 65°C (Association of Official Analytical Chemists, 1970). The PR-solution mixture was filtered through No. 5 Whatman filter paper (first extraction); the residue was extracted again with 100 mL of fresh neutral ammonium citrate solution (second extraction) and filtered. An aliquot (1 mL) of each filtrate was digested on a hotplate with 2 mL of perchloric acid in a 50-mL beaker covered with a watch glass until clear white salts or colorless solution remained and dense white fume appeared. The beaker was cooled and deionized water was added and the contents of the beaker were transferred to a 100-mL volumetric flask where the volume was made. The solution thus obtained was analyzed for

inorganic P in a 25-mL volumetric flask using the heteropoly blue colorimetric method described by Murphy and Riley (1962) after neutralization with 5N NaOH by using p-nitrophenol as an indicator. Absorbance was measured at 880 nm by using a Model 552 Perkin-Elmer double-bean UV-visible spectrophotometer (Perkin-Elmer, Coleman Instruments Division, Oak Brook, IL).

Extraction with ammonium citrate, pH 3, 2% citric acid, and 2% formic acid

A 0.2-g PR sample was equilibrated with 20 mL of ammonium citrate, pH 3 (unpublished method, personal communication, IFDC-TVA), 2% citric acid (Association of Official Analytical Chemists, 1960), or 2% formic acid (Hoffman and Mager, 1953) for 1 h at room temperature in a 50-mL plastic centrifuge tube. The PR-solution mixture was centrifuged at 10,000 x g for 5 min and passed through a 0.45-μm membrane filter (Micron Separations, Inc., Westboro, MA). An aliquot (1-2 mL) of the filtrate thus obtained was digested on a hotplate with 2 mL of perchloric acid in a 50-ml beaker covered with a watch glass. The contents were then transferred into a 100-mL volumetric flask, and the volume was adjusted to 100 mL with deionized water. The solution was analyzed for inorganic P in a 25-mL volumetric flask in the same manner as in the previous paragraph.

Trace Metal Contents

In determination of the trace metal contents of the PR samples, 2 g PR sample was placed in a 100-mL Teflon beaker covered with a watch glass and digested on a

hotplate as described by Bureau (1982) and modified by Basta and Tabatabai (1990). In this modification, 5 mL concentrated HNO_3 was added to the sample and heated to near dryness. The beaker was cooled down and 6 mL of $HClO_4$ was added to the residue; the contents were heated until a colorless residue was obtained. After the sample had cooled down, 5 mL of HF was added and the contents were subsequently heated until the appearance of $HClO_4$ fumes. The HF treatment was repeated to ensure complete dissolution of silicate minerals. The contents of the beaker were transferred into a 50-mL volumetric flask, and the volume was made with deionized water. The content of the volumetric flask was then transferred to a 100-mL polyethylene bottle to which 5.6 g of H_3BO_3 was added. The bottle was shaken several times and then filtered through a 0.45-μm membrane filter (Micron Separations, Inc., Westboro, MA). Nineteen metals (Al, Ca, K, Na, Mg, Ba, Cd, Co, Cu, Cr, Cs, Fe, Li, Mn, Ni, Pb, Rb, Sr, and Zn) of the acid digest was determined by flame atomic absorption spectrophotometry (AA) by using a Perkin-Elmer Model 5000 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Assessment of reactivity and trace metal contents of a PR are important steps in evaluating its agronomic potential. It is not the intent of this part to link reactivity of a PR to its trace metal contents; therefore, the two topics will be discussed separately.

Reactivity of Phosphate Rocks

Two methods were used to evaluate the reactivity of the 12 phosphate rocks used in this work. The results obtained will be discussed under subheadings according to the methods employed.

X-ray characterization

The x-ray powder diffraction patterns of carbonate apatite occurring in PR were characteristic to apatite with slight shifts in position of peaks and intensities, indicating changes in the cell parameters (patterns not shown). These changes occurring in carbonate content affect the unit-cell a dimension of apatite structure (Smith and Lehr, 1966); Lehr, 1967; McClellan and Lehr, 1969). The work of Smith and Lehr (1966) established a relationship between the unit cell a dimension of apatite and carbonate content. Models developed by McClellan (1980) showed that the major substitutions in mineral francolites can be estimated by a single parameter; which is the a axis length. The length of the a axis of the 12 phosphate rocks under study was obtained by x-ray and compiled in Table 3. The results of measurement of the unit-cell a dimension of the PRs show that the values ranged from 9.324 Å for North Carolina PR to

Table 3. Empirical formulae of phosphate rocks studied

Phosphate rock	Length of a axis(Å)	Empirical formula[a]
Kodjari	9.361	$Ca_{9.92}Na_{0.06}Mg_{0.02}(PO_4)_{5.75}(CO_3)_{0.25}F_{2.10}$
Tahoua	9.365	$Ca_{9.96}Na_{0.03}Mg_{0.01}(PO_4)_{5.87}(CO_3)_{0.13}F_{2.05}$
North Carolina	9.324	$Ca_{9.55}Na_{0.32}Mg_{0.13}(PO_4)_{4.83}(CO_3)_{1.17}F_{2.47}$
Gafsa	9.327	$Ca_{9.58}Na_{0.30}Mg_{0.12}(PO_4)_{4.89}(CO_3)_{1.11}F_{2.44}$
Khourigba	9.336	$Ca_{9.67}Na_{0.24}Mg_{0.09}(PO_4)_{5.09}(CO_3)_{0.91}F_{2.36}$
Tilemsi Valley	9.359	$Ca_{9.90}Na_{0.07}Mg_{0.03}(PO_4)_{5.69}(CO_3)_{0.31}F_{2.12}$
Central Florida	9.336	$Ca_{9.67}Na_{0.24}Mg_{0.09}(PO_4)_{5.09}(CO_3)_{0.91}F_{2.36}$
Sechura	9.337	$Ca_{9.03}Na_{0.74}Mg_{0.09}(PO_4)_{4.88}(CO_3)_{1.12}F_{1.73}(OH)_{0.72}$
Minjingu	9.353	$Ca_{9.84}Na_{0.11}Mg_{0.13}(PO_4)_{5.52}(CO_3)_{0.48}F_{2.19}$
North Florida	9.336	$Ca_{9.67}Na_{0.24}Mg_{0.09}(PO_4)_{5.09}(CO_3)_{0.91}F_{2.36}$
Hahotoe	9.354	$Ca_{9.85}Na_{0.11}Mg_{0.04}(PO_4)_{5.55}(CO_3)_{0.45}F_{2.18}$
Parc W	9.357	$Ca_{9.88}Na_{0.09}Mg_{0.03}(PO_4)_{5.63}(CO_3)_{0.37}F_{2.15}$

[a]With the exception of the unit-cell a dimension of PR samples from Sechura and Minjingu which were obtained from Chien and Hammond (1978a) and Van Kauwenbergh (1985), respectively, all other unit a dimensions and the empirical formulae were calculated from x-ray diffraction data and statistical models of francolites as established by McClellan and Lehr (1969), McClellan (1980), and McClellan and Van Kauwenbergh (1990).

9.365 Å for Tahoua PR. The unit-cell a dimension value obtained for each rock is close to published values. Hammond et al. (1986) published unit-cell a dimension values of 9.351, 9.328, 9.322, and 9.345 Å for Hahotoe, Gafsa, North Carolina, and Central Florida, respectively. These differences in the a dimension values are related to the degree of alteration of the ores in the deposit. For example, the lateritically altered near-surface ores of Hahotoe deposit in Togo have francolites with unit-cell a

dimension values of 9.353 Å, whereas those recovered from cores in the unweathered ore contain francolites with a values of 9.340 Å (McClellan, 1980). The fundamental substitution in sedimentary francolites is the substitution of CO_3^{2-} for PO_4^{3-}. Consequences of increasing substitution are a decrease in unit-cell a dimension, a decrease in crystallite size, and an increase in the specific surface area of the apatite aggregates (McClellan and Lehr, 1969). Therefore, high reactive PRs would be highly substituted francolites with a unit-cell a dimension close to 9.322 Å. On the other hand, low reactive PRs would be the least substituted francolites with a unit-cell a dimension close to 9.376 Å for zero substitution (McClellan and Gremillion, 1980). The empirical formula of each of the rocks studied is shown in Table 3 and suggests that apatite in sedimentary PR can be adequately described by their Ca, Na, Mg, P, CO_2, and F contents.

Chemical reactivity

The x-ray characterization method measures the actual thermodynamic stability of the apatite structure and is considered the most appropriate means of characterizing PR reactivity (Hammond et al., 1986). This method, however, requires sophisticated equipment that is not available in many laboratories. Rapid laboratory dissolution tests have been, therefore, devised for determining PR reactivity. There is no standardized method for analyzing PR reactivity and various extractants have been used to determine PR reactivity.

Four extractants (the most commonly used) were used in the work reported here: neutral ammonium citrate (pH 7), ammonium citrate (pH 3), 2% formic acid, and 2% citric acid. The percentage of P extracted by each of the extractants from each of the rocks is compiled in Table 4. Because of their different properties, the five methods used extracted different amounts of P. These differences may cause confusion in interpreting and comparing PRs. With the exception of Sechura PR, the percentage of P extracted by the neutral ammonium citrate is very low compared with that extracted by other extractants. Moreover, these results suggest that the P extracted by the neutral ammonium citrate was underestimated, because part of the extractant was consumed by the accessory gypsum, calcite, or dolomite present in the rocks. Ammonium citrate (pH 3) and 2% formic acid produced very similar results and were used with x-ray data to classify the PRs according to their reactivity (Table 5). The large difference observed in the amounts of P extracted by the extractants suggests that the chemical solubility tests are not good enough to rank PRs according to their reactivity and must be coupled with x-ray analysis and agronomic field trials. Figures 1 and 2 show the relationships between apatite composition and solubility test value by various extractants. Among the extractants used, only neutral ammonium (first extraction) and 2% formic acid significantly correlated with the unit-cell a dimension of the apatite ($p < 0.05$). A review by Hammond et al. (1986) on the agronomic value of unacidulated and partially acidulated PRs indigenous to the tropics concluded that expression of soluble P as a percentage of rock, rather than as a percentage of total P,

Table 4. Reactivity scales of the phosphate rocks studied as measured in various extractants

Phosphate rock	Neutral ammonium citrate[a] 1st	Neutral ammonium citrate[a] 2nd	pH 3 Ammonium citrate	2% Formic acid	2% Citric acid
	%P in PR				
Kodjari	0.67	0.64	3.42	2.88	2.86
Tahoua	0.72	0.82	3.54	2.95	2.70
North Carolina	2.74	2.54	9.35	11.4	5.98
Gafsa	1.35	1.45	8.28	10.4	5.24
Khourigba	1.54	1.16	7.98	9.44	5.32
Tilemsi Valley	2.10	2.05	8.12	6.90	5.40
Central Florida	1.98	1.84	5.79	4.00	3.09
Sechura	1.83	0.83	11.1	11.1	6.56
Minjingu	1.77	1.49	11.9	10.5	6.55
North Florida	2.14	2.04	5.89	4.16	3.85
Hahotoe	0.90	1.06	4.71	3.64	3.21
Parc W	0.35	0.48	3.69	1.92	2.76

[a]First and second extractions.

Table 5. Reactivity of the phosphate rocks studied

Deposit	Reactivity
Sechura	High
Minjingu	High
Gafsa	High
North Carolina	High
Tilemsi Valley	Medium
Khourigba	Medium
Central Florida	Medium
North Florida	Medium
Kodjari	Low
Parc W	Low
Tahoua	Low
Hahotoe	Low

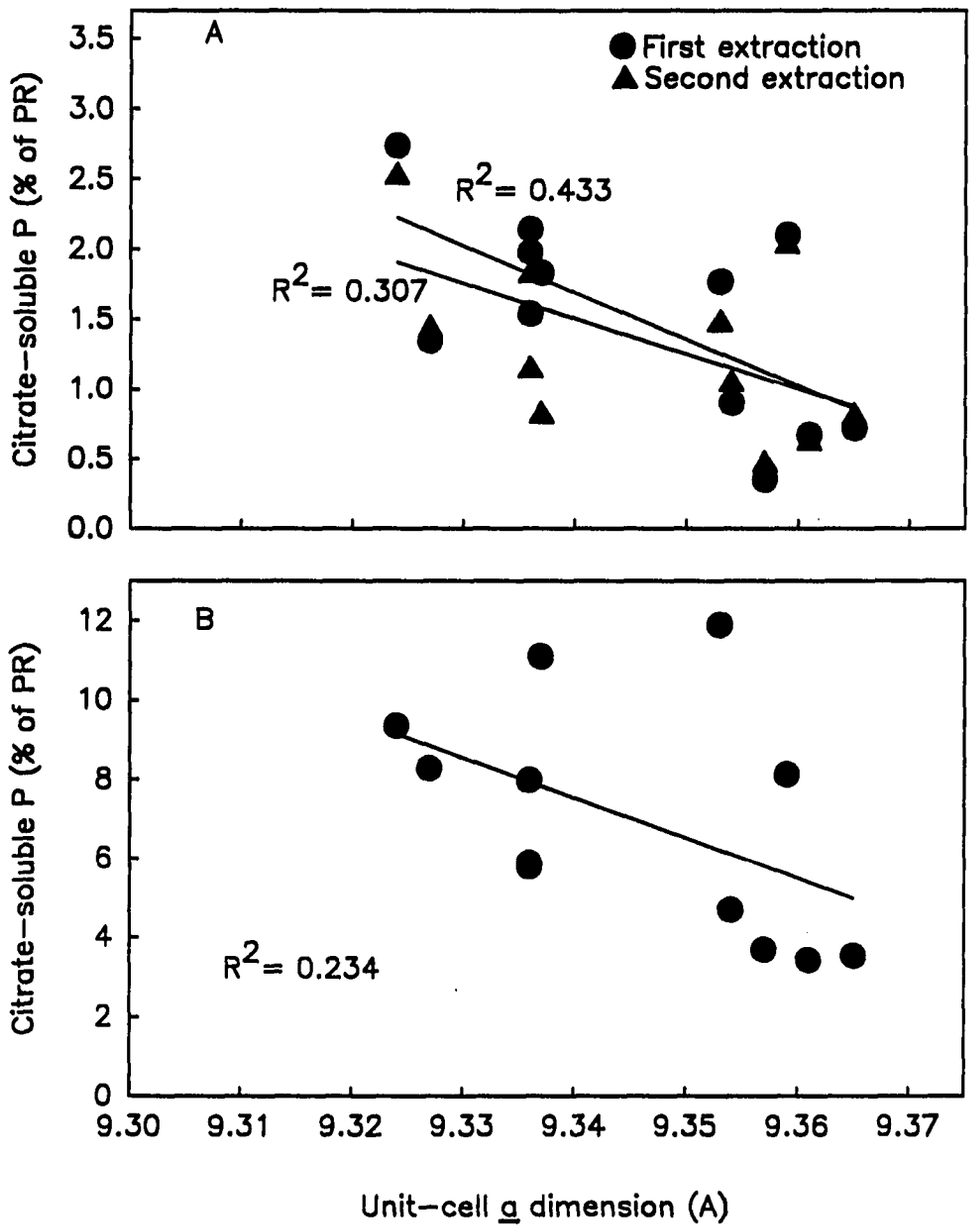


Figure 1. Relationships between neutral ammonium citrate solubility (A) and pH3 ammonium citrate solubility (B) of apatite and its composition as indicated by unit-cell a dimension

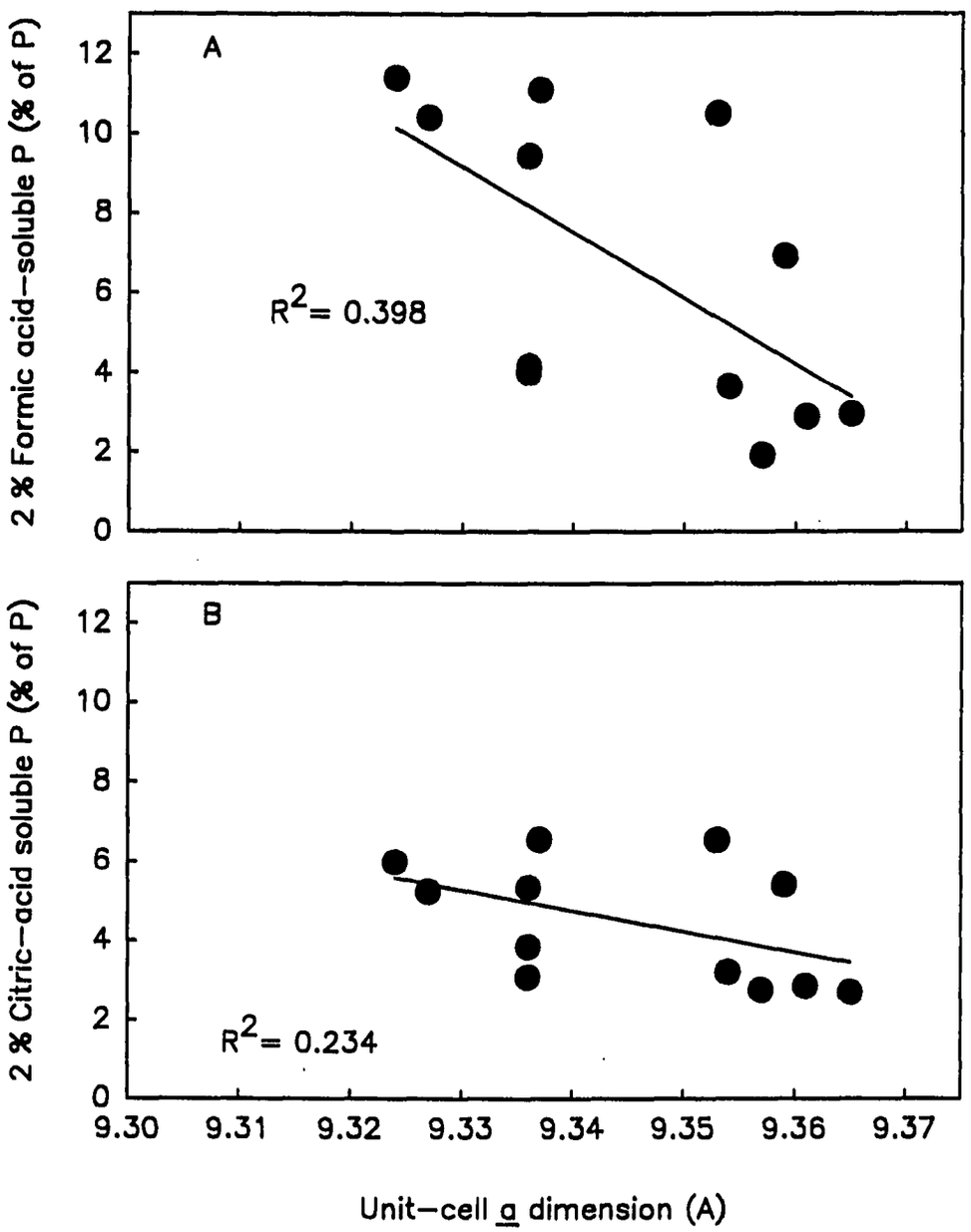


Figure 2. Relationships between 2% formic acid solubility (a) and 2% citric acid solubility (B) of apatite and its composition as indicated by unit-cell a dimension

is preferable where the PR sources vary widely in P content. Therefore, the results obtained in this work are expressed as percentages of the PRs used instead of percentage of total P in the PRs. The other extractants may have overestimated the P extracted because of the presence in the rock of acid-soluble Al phosphate (Lehr and McClellan, 1972).

Trace Metal Contents

Although PRs are mainly known for their P content, they contain various amounts of trace and nontrace metals. Addition of these rocks to soils may result in accumulation of trace metals at levels exceeding their natural abundance in soils. In the context of this work, the term "trace metal" refers to metals that, when present in sufficient concentration may be toxic to living organisms. Ten trace metals and nine nontrace metals of 12 PRs of various deposits were determined. Results are compiled in Tables 6 and 7. Table 6 shows that the analyzed PR samples varied greatly with respect to their trace metal contents. Three groups of metals may be easily identified according to the amounts of these metals present: the first group contains metals that appear in relatively large amounts: Cr, Mn, and Zn; the second contains metals that occur in moderate amounts: Cd, Co, Cu, Ni, and Pb; the third and last group contains metals that occur in relatively small amounts: Li and Rb. Manganese appears to be the most abundant; its concentration in the PR samples ranged from 6553 mg kg^{-1} in Tilemsi Valley PR to only 22 mg kg^{-1} in Khourigba PR with a mean of 1041 mg kg^{-1} and a median of 263 mg kg^{-1} PR. Manganese content of Tahoua PR (3910 mg kg^{-1})

Table 6. Total trace metal composition of phosphate rocks studied

Phosphate rock	Trace metal									
	Cd	Co	Cu	Cr	Li	Mn	Ni	Pb	Rb	Zn
	mg kg^{-1}									
Kodjari	6	20	6	19	6	456	3	20	18	54
Tahoua	10	104	7	19	4	3910	26	20	5	139
North Carolina	42	22	8	137	3	24	12	9	5	332
Gafsa	45	21	8	165	2	25	8	11	4	576
Khourigba	13	22	29	244	2	11	23	40	4	228
Tilemsi Valey	7	41	36	21	2	6553	61	19	8	101
Central Florida	11	23	6	45	2	282	6	11	6	108
Sechura	22	6	9	90	3	78	12	7	7	91
Minjingu	9	23	17	18	9	523	6	16	16	299
North Florida	10	20	5	47	2	266	6	9	7	91
Hahotoe	47	25	41	97	2	102	20	43	3	339
Parc W	5	25	8	331	2	261	1	7	3	88
Median	10	22	8	46	2	263	10	14	6	124
Mean	19	30	15	78	3	1041	15	18	7	204

was among the high values obtained. Rubidium content ranged from 3 mg kg^{-1} in Hahotoe PR to 18 mg kg^{-1} in Kodjari PR. The concentrations of Cu and Ni found in the PRs do not vary greatly; the mean and the median values were 15 and 8 for Cu and 15 and 10 mg kg^{-1} for Ni, respectively; Hahotoe Pr contained the greatest concentration of Cu (41 mg kg^{-1}), whereas Tilemsi Valley PR contained the greatest concentration of Ni (61 mg kg^{-1}). Three samples: Hahotoe, Gafsa, and North Carolina PRs

can be highlighted for their Cd content; 47, 45, and 42 mg kg^{-1}, respectively. These same samples contain the greatest concentration of Zn: 576 mg kg^{-1} in Gafsa PR, 339 mg kg^{-1} in Hahotoe PR, and 332 mg kg^{-1} in North Carolina PR. Hahotoe and Khourigba PRs contained about twice the concentration of Pb found in Kodjari and Tahoua PRs.

The nontrace metal contents of the PRs studied are shown in Table 7. Kodjari PR contains the greatest concentration of Al (20 g kg^{-1}), whereas North Carolina PR contained a little less than 2 g kg^{-1}. Although Ca constitutes the back-bone of apatite structure, its concentration varied from 330 g kg^{-1} in Khourigba PR to 211 g kg^{-1} in Kodjari PR. Due to the great concentrations of Ca present in PRs, Hellums et al. (1989) investigated the potential use of PRs as sources of Ca for crop production. Potassium in the PR samples was as low as 0.3 g kg^{-1} in Hahotoe PR and as high as 11 g kg^{-1} in Minjingu PR, with a mean and a median of 2.9 and 1.4 mg kg^{-1}, respectively. Sodium and Sr contents showed means and medians, respectively, of 10.7 and 10.4 mg kg^{-1} for Na and 1.6 and 1.05 for Sr. Iron was found in substantial concentrations, varying greatly from 46 g kg^{-1} in Tahoua PR to 1.4 g kg^{-1} in Khourigba PR. Barium was also present in significant concentrations in Minjingu PR (4.4 g kg^{-1}); at the detection limit of 10 mg/mL, no Ba was found in the North Carolina, North Florida, and Hahotoe PRs (Table 7). Similarly, no Cs was detected in any of the PR samples at 1 mg/mL detection limit. Literature on trace and nontrace metal contents of PRs is seriously lacking. Arora et al. (1975) studied 14 elements in a PR

Table 7. Nontrace metal composition of phosphate rocks studied

Phosphate rock	Nontrace metal							
	Al	Ba[a]	Ca	Fe	K	Mg	Na	Sr
	g kg^{-1}							
Kodjari	20.0	3.5	211	18.9	7.9	5.9	12.2	0.7
Tahoua	9.0	0.2	261	45.7	0.8	0.6	4.4	1.0
North Carolina	1.7	0	310	4.1	0.8	1.8	1.0	2.4
Gafsa	2.0	0.3	313	1.6	1.0	2.6	12.3	1.9
Khourigba	2.0	0.4	330	1.4	0.7	1.1	8.5	0.8
Tilemsi Valley	10.0	2.5	268	43.4	3.4	5.3	9.9	1.0
Central Florida	4.0	2.2	294	7.8	3.4	1.4	7.4	1.1
Sechura	5.0	3.5	218	1.9	3.6	6.5	22.1	1.7
Minjingu	9.0	4.4	292	7.1	10.9	16.9	22.8	6.7
North Florida	12.6	0	322	3.9	1.8	4.8	12.2	1.0
Hahotoe	5.7	0	305	7.7	0.3	0.6	4.2	0.3
Parc W	5.5	0.4	301	6.5	0.4	0.7	10.9	1.1
Median	5.6	0.4	298	6.8	1.4	2.2	10.4	1.0
Mean	7.2	1.5	285	12.5	2.9	4.0	10.7	1.6

[a]0, Indicates values below the detection limit of 0.02 μg Ba/ml.

sample, but the source of sample that they used was not specified. Their results cannot be used for comparison because metal contents in PRs vary considerably. The results reported suggest that besides the elements that appear in the empirical formula of apatite, other elements such as Al and Fe are present in substantial quantities in some PRs (Kodjari, Tahoua, and Tilemsi PRs). The form in which these elements are found

in PR (either bound to P or Al/Fe oxides) may play a determinant role in release of inorganic P from these rocks by organic acids. The amount of inorganic P released will, therefore, be a result of interaction among all these 19 elements identified in PRs.

Phosphate rocks remain the only important source of production of P fertilizers in the commercial fertilizer industry. It is obvious that the trace metals present in PR are incorporated into commercial P fertilizers sold around the world. The concentrations of these metals in P fertilizers will reflect, therefore, the original concentration of the metals in the PR, but will vary significantly from one P fertilizer to another and within the same P fertilizer group. A recent study by Charter et al. (1993) provided evidence that among the eighteen elements detected in PRs, fifteen were found in 72 samples of P fertilizers sold in Iowa. The elements not detected in these P fertilizers were Ba, Li, and Rb. The concentration of elements in the P fertilizers, however, varied considerably, because these fertilizers were produced from PRs of various origins. This variation in trace metal contents of these P fertilizers justified the need to assess each PR individually.

PART II. EFFECT OF ORGANIC ACIDS ON PHOSPHOROUS RELEASE FROM PHOSPHATE ROCKS

INTRODUCTION

During the last four decades, interest in direct application of PR has grown and has focused on developing reliable and inexpensive means to make PR more soluble. A number of low-molecular-weight (LMW) organic acids have been identified in the soil rhizosphere and it was confirmed that these organic acids play a great role in the dynamics of nutrient elements in soils. The reaction between LMW organic acids and phosphate rock is of interest because of the role of the former in soil weathering and soil forming processes. The effectiveness of an organic acid to release P from PR depends not only on the chemical structure of the acid but also on internal factors of the PR. One such factor is the free carbonate content of sedimentary phosphate rocks. A large amount of carbonate in PR constitutes a problem in the solubility test because carbonate depresses P extraction from the rock. LMW organic acids have the ability to solubilize phosphate from phosphate-bearing minerals by reacting with polyvalent metals (mainly Ca) in the minerals. However, their action is primarily limited by the carbonate content of PR. When organic acids are added to PR containing substantial amounts of free carbonate, part of the acid is consumed by the carbonate and only a small amount of inorganic phosphate is released into solution. The release of phosphate can be increased by removing the free carbonate from the rock with triammonium citrate solution (pH 8.1 $\pm$ 0.1) before P extraction. Little information is available, however, on the dissolution of PR by low concentrations of LMW organic acids, on the effect of free carbonate removal on phosphate release from PRs, and on

the relationship between P and Ca, Mg, Al and Fe released by each organic acid. Such information is needed for developing better strategies to increase plant-available P in soils. Therefore, the objectives of this part of the study were: (1) to assess the influence of equilibration time on P release from PR extracted with organic acids, (2) to evaluate the P release from the PRs by several organic and mineral acids, (3) to evaluate the influence of free carbonate content on P release from PRs by selected organic and sulfuric acids, and (4) to establish the relationship between the P and each of Ca, Mg, Al, and Fe released from various PRs.

MATERIALS AND METHODS

Phosphate Rocks

The PRs included in this study were those used in part I. Total carbonate content of the samples was determined by treating 5 g of ground PR sample (<200 mesh) with 20 mL HCl (2 M) as outlined by Bundy and Bremner (1972).

Procedures

In studying the P released from PR by acids and the effect of equilibration time on P release, three mineral acids (hydrochloric, nitric, and sulfuric) and 19 organic acids (glycolic, pyruvic, oxalic, malonic, fumaric, maleic, succinic, oxalacetic, malic, α-ketoglutaric, tartaric, cis-aconitic, citric, salicylic, p-hydroxybenzoic, protocatechuic, phthalic, vanillic, and gallic) were used (Table 8, and Table 24, Appendix). Appropriate amounts of a reagent-grade of these acids were dissolved in deionized water to give 1 or 10 mM. The pH values were measured (Table 9) and a 1-g sample of PR was equilibrated with 25 mL of acid (1 mM or 10 mM) in a 50-mL plastic centrifuge tube at 25°C±1°C for 24 h or various times in a Model G26 New Brunswick incubator shaker (New Brunswick Scientific Co., Inc., New Brunswick, NJ). The PR-solution mixture was centrifuged at 10,000 x g for 5 min and filtered through a 0.45-μm membrane filter. The filtrate thus obtained was analyzed for inorganic P in a 25-mL volumetric flask as described in part I.

Table 8. Physical constants of the mineral and organic acids used

Acid	Molecular formula	Molecular weight	pK
	Mineral acids		
Hydrochloric	HCl	36.47	-6.1
Nitric	HNO_3	63.02	-1.43
Sulfuric	H_2SO_4	98.08	pK_2 = 1.99
	Organic acids		
Aliphatic acids			
Glycolic	$HOCH_2COOH$1	76.05	3.832
Pyruvic	$CH_3COCOOH$	88.06	2.49
Oxalic	HOOCCOOH	90.04	pK_1 = 1.23 pK_2 = 4.19
Malonic	$CH_2(COOH)_2$	104.16	pK_1 = 2.83 pK_2 = 5.69
Fumaric	trans-HOOCCH=CHCOOH	116.07	pK_1 = 3.03 pK_2 = 4.44
Maleic	Cis-HOOHCH=CHCOOH	116.07	pK_1 = 1.83 pK_2 = 6.07
Succinic	$HOOCCH_2CH_2COOH$	118.09	pK_1 = 4.16 pK_2 = 5.61
Oxalacetic	$HOOCCOCH_2COOH$	132.10	pK_1 = 2.56
Malic	$HOOCCH(OH)CH_2COOH$	134.10	pK_1 = 3.40 pK_2 = 5.11
α-Ketoglutaric	$HOOCCH_2CH_2COCOOH$	146.10	-
Tartaric	HOOCCH(OH)CH(OH)COOH	150.09	pK_1 = 2.98 pK_2 = 4.34
Cis-Aconitic	$HOOCCH_2C(COOH)=CHCOOH$	174.11	pK_1 = 2.80 pk_2 = 4.46
Citric	$HOC(CH_2COOH)_2COOH$	192.14	pK_1 = 3.14 pK_2 = 4.77 pK_3 = 6.39
Aromatic acids			
Salicylic	HOC_6H_4COOH	138.12	pK_1 = 2.98 pK_2 =13.40
p-Hydroxybenzoic	HOC_6H_4COOH	138.13	pK_1 = 4.59 pK_2 = 9.30
Protocatechuic	$(HO)_2C_6H_3COOH$	154.10	-
Phthalic	$C_6H_4(COOH)_2$	166.13	pK_1 = 2.89 pK_2 = 5.51
Vanillic	$CH_3OC_6H_3(OH)COOH$	168.16	-
Gallic	$(HO)_3C_6H_2COOH$	170.10	pK_1 = 4.43 pK_2 = 9.11 pK_3 =11.38

Table 9. pH values of the mineral and organic acids used

Acid	pH value	
	1 mM	10 mM
None (water control)[a]	5.34	5.34
Mineral acids		
Hydrochloric	3.13	2.21
Nitric	3.03	2.11
Sulfuric	3.08	2.24
Organic acids		
Aliphatic acids		
Glycolic	3.48	3.03
Pyruvic	3.18	2.49
Oxalic	3.15	2.35
Malonic	3.21	2.62
Fumaric	3.24	2.68
Maleic	3.10	2.36
Succinic	3.63	3.19
Oxalacetic	3.12	2.47
Malic	3.35	2.86
α-Ketoglutaric	3.12	2.45
Tartaric	3.24	2.72
Cis-Aconitic	3.14	2.43
Citric	3.26	2.73
Aromatic acids		
Salicylic		
p-Hydroxybenzoic	3.26	2.67
Protocatechuic	3.79	3.38
Phthalic	3.77	3.30
Vanillic	3.23	2.65
Gallic	3.74	3.27

[a]pH value of the deionized water used.

In studying the effect of carbonate removal on P released, 1.5 g of PR sample was equilibrated with 100 mL of 0.5 M triammonium citrate (pH 8.1±0.1) as described by Silverman et al. (1952). This was done by adding 100 mL of the extractant to 1.5 g of PR in a 125-mL Erlenmeyer flask, and digesting for 4 h at 65°C±1°C in a water bath unit, model MSB-1122A-1 (Blue M Electric Co., Blue Island, IL) with constant agitation after which the mixture was allowed to stand at room temperature for 18 h. The supernatant was decanted and 100 mL fresh triammonium citrate (p.5 M) solution was added to the residue and digested for four additional hours, after which the flask was allowed to stand at room temperature for 18 h, followed by filtration of the mixtures through a 0.45-μm membrane filter. The residue on the membrane filter was washed several times with deionized water and dried at room temperature for 48 h. One gram of the washed sample was equilibrated with 25 mL of equimolar concentration (10 mM) of each of nine organic acids (citric, cis-aconitic, oxalic, tartaric, malonic, fumaric, pyruvic, salicylic, or glycolic) or sulfuric acid. In testing the P release from PR before and after free carbonate removal, a 1-g sample (washed or not washed) in a 50-mL plastic centrifuge tube was equilibrated at 25°C±1°C in a New Brunswick incubator-shaker with 25 mL of 10 mM acid for 24 h, centrifuged and filtered (0.45-μm membrane filter). The filtrate thus obtained was analyzed for inorganic P by a heteropoly blue method (Murphy and Riley, 1962) and for Ca, Mg, Fe, and Al by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Influence of Extraction Time on Phosphorous Release

Because there are no published data on the release of P from PRs with organic acids, it was essential first to determine the equilibration time which would correspond to an optimum release of P from the rocks. For this purpose, each PR sample was equilibrated at 25°C±1°C with 25 mL of 1 mM citric acid for various times. Results showed that the amount of P released varied widely with time and among the rocks studied. From the results obtained, the PRs could be divided into four divergent groups. The first group consisted of Tahoua, Central Florida, and North Florida PRs. In this group, the P release reached a maximum after 8 h of equilibration time and then decreased gradually with increasing equilibration time (Figure 3). This group included two of the four medium reactive PRs (Central Florida and North Florida). The amounts of P released from Tahoua PR was lower at all equilibration times than those released from the other rocks; after 48 hours equilibration, the P released was about 28 mg P kg^{-1} PR.

The second group of PRs included Gafsa, Khourigba, Sechura, and Minjingu PRs (Figure 3). Three PRs (Gafsa, Sechura, and Minjingu) of this group are high reactive PRs. The maximum P released for this group was at 30 min of equilibration (about 20 mg P kg^{-1} for Gafsa PR). The P released then decreased sharply with increasing equilibration time and reached 1 mg P kg^{-1} at 48 h.

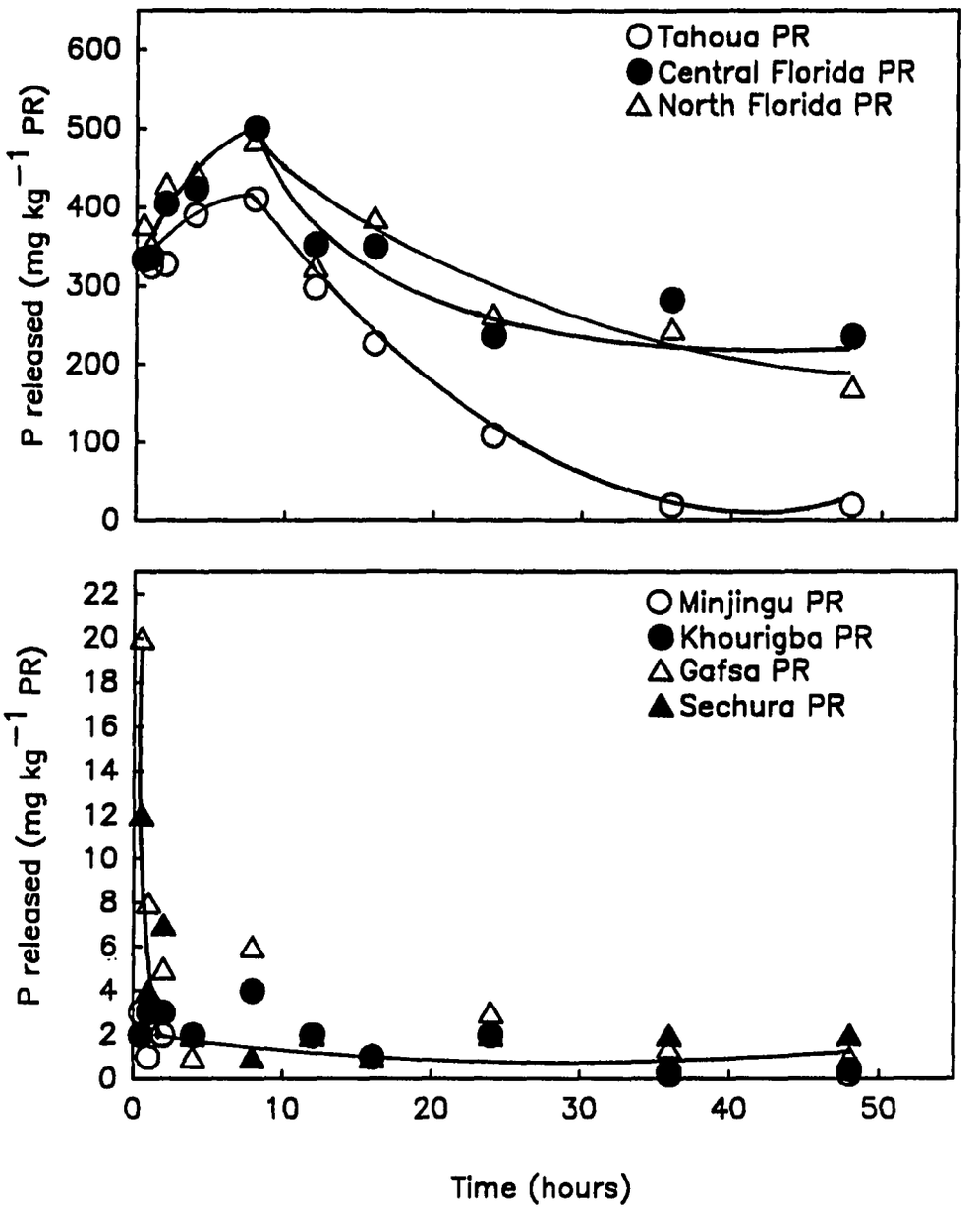


Figure 3. Effect of equilibration time on the release of phosphorus from Tahoua, Central Florida, and North Florida, phosphate rocks by 1 mM citric acid

The third group identified included North Carolina and Tilemsi valley PRs and had solubility patterns similar to those of the second group, but with greater P released (Figure 4). The fourth group included three low reactive PRs (Kodjari, Hahotoe, and Parc W). For this group, 24 h equilibration time was adequate for maximum P release (Figure 4). The P released from Parc W PR (875 mg kg^{-1}) was higher at all times than those released from other PRs, whereas Kodjari PR released the lowest P at all equilibration times.

At high concentration (25 mM), some organic acids may interfere with the development of the heteropoly blue using the method of Murphy and Riley (1962) in determining inorganic P in solution. Experiments in our laboratory, however, have shown that none of the acids used (including citric acid) interfered with color development at 1 or 10 mM concentration (Harrold, 1992). Interference in color development is, therefore, unlikely to explain the results obtained during these experiments. Phosphorous extraction with organic acids at low concentration (1 mM) may have been depressed by free carbonates contained in the rocks. Minjingu, Khourigba, Gafsa, Sechura, and North Carolina PRs contain substantial amount of free carbonate and released the lowest amount of P (Figures 3 and 4). Because free carbonates are more soluble than apatite (Silverman et al., 1952), only small portion of P was released into solution. Kodjari, Parc W, and Hahotoe PRs contained small amounts of free carbonates (Table 1) and, therefore, released more P than other PRs. No single equilibration time appeared to be satisfactory for all the rocks; a uniform equilibration time of 24

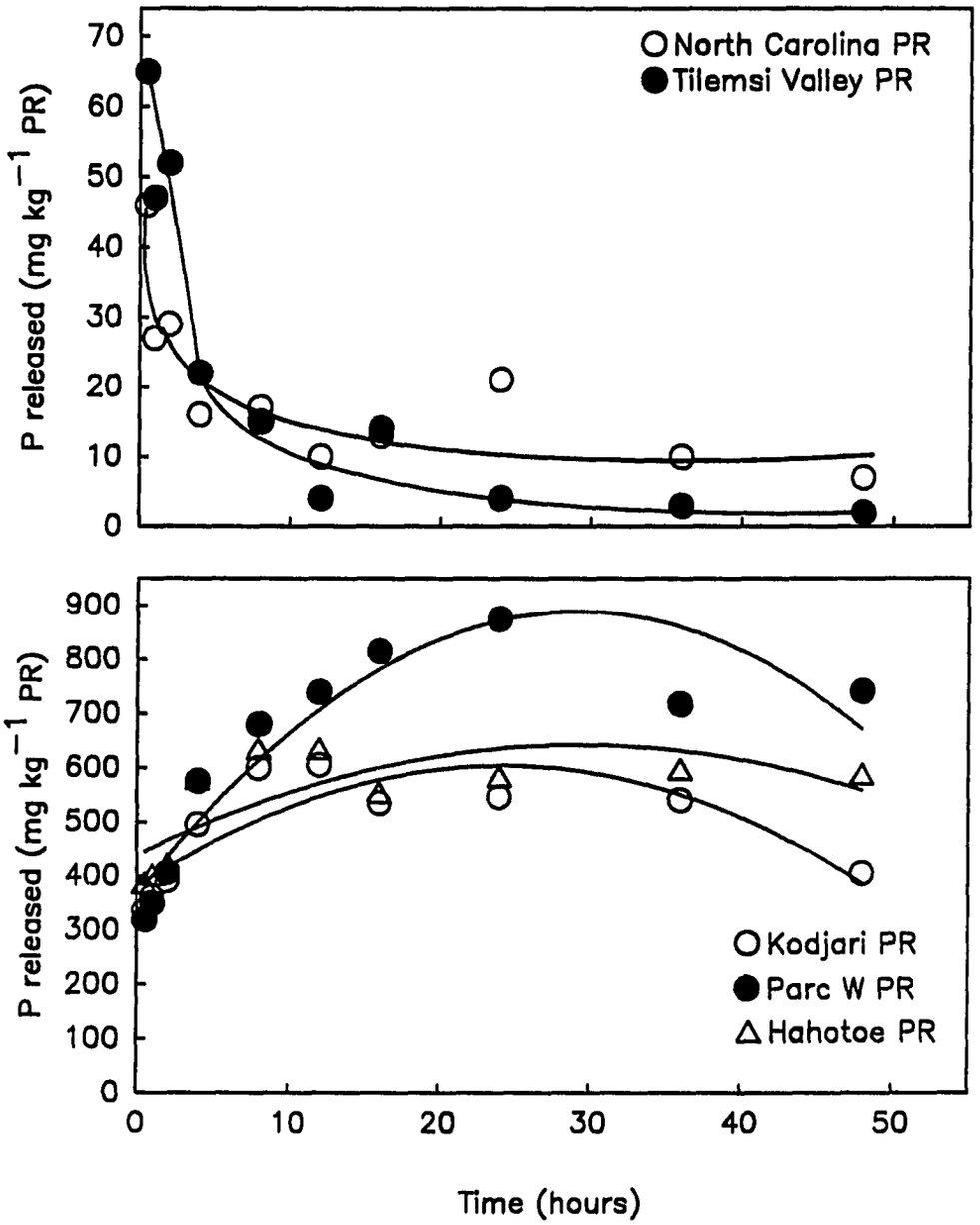


Figure 4. Effect of equilibration time on the release of phosphorus from North Carolina, Tilemsi, Kodjari, Parc W, and Hahotoe phosphate rocks by 1 mM citric acid

hours was, therefore, chosen for studies to assess P release from PRs with mineral and organic acids.

Release of Phosphorus from Phosphate Rocks

The release of P from PRs was studied by using two PRs (Kodjari and North Florida) and 22 acids. The acids included 19 organic (13 aliphatic and 6 aromatic acids) and three mineral (sulfuric, nitric, and hydrochloric acids) acids at equimolar concentration of 1 or 10 mM. Figure 5 shows the effect of 1 mM organic or mineral acid on the release of P from two PRs. The P released from Kodjari PR was greater than that released from North Florida PR with each of the acids tested, suggesting that free carbonate content in North Florida PR possibly depressed P extraction. Indeed, when acid is added to a phosphate rock containing substantial amounts of free carbonate, part of the acid is consumed by the carbonate and only a small portion of the acid reacts with the rock. The consequence of this was that only small amounts of P were released from the PR. It is possible to recognize two groups of acids corresponding to two types of actions: the mineral acid group with mainly acid effect and the organic acids containing carboxylic groups with acid and complexing actions. Further subdivision can be made within the carboxylic acid group: the tricarboxylic acid subgroup (citric and cis-aconitic), the dicarboxylic acid subgroup (oxalic, tartaric, malonic, fumaric, malic, α-Ketoglutaric, phthalic, maleic, oxalacetic, and succinic) and the monocarboxylic acid subgroup. The amounts of P released with the organic acids varied greatly, ranging from 500 mg P kg^{-1} PR for citric acid to about 50 mg P kg^{-1}

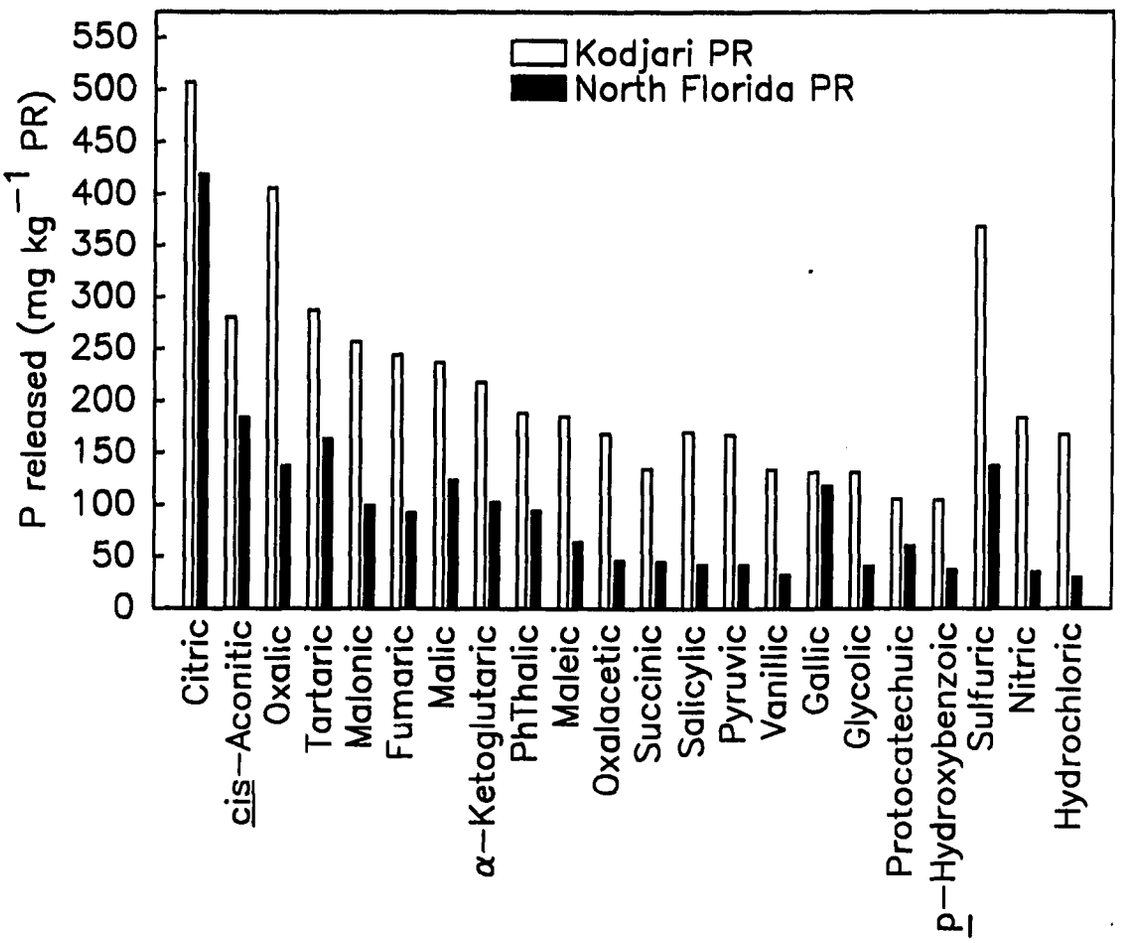


Figure 5. Effect of 1 mM organic or mineral acids on the release of phosphorus from Kodjari and North Florida phosphate rocks

PR for p-hydroxybenzoic acid. Citric acid, oxalic acid and sulfuric acid appeared to be the most effective in P release.

The position and type of functional groups within each carboxylic group appeared to be the dominant factor that influence the amount of P released. For example, both citric and cis-aconitic acids have α-, β-, and γ-carboxyl groups and a β-hydroxyl group on citric acid. Consequently, the amount of P released by citric acid (about 500 mg P kg^{-1} PR) from Kodjari PR was almost double the amount of P released by cis-aconitic acid (254 mg P kg^{-1} PR) from the same Kodjari PR (Figure 5). This suggested an active participation of the OH group during the P release process. Within the dicarboxylic acid group, oxalic acid was the most effective by releasing an amount of P (about 400 mg P kg^{-1} PR) slightly greater than the amount released by sulfuric acid from Kodjari PR. For dicarboxylic acids the closeness of the two COOH group is a very important factor to be considered; the more the COOH groups are separated from each other, the harder the chelation process (Razzaagbe-Karimi and Robert, 1975). This explains why oxalic acid (two COOH groups next to each other) was more effective than succinic acid, which has the two COOH groups separated by two CH_2 groups. The number of OH groups in the dicarboxylic acid group also has an important role because tartaric acid (with two OH) was more effective than malic acid (with one OH group). Among the aromatic acids studied, alicyclic and pyruvic acids appeared to be the most effective. As the hydroxyl group is removed further from the carboxyl group on the ring (e.g., protocatechuic and p-hydroxybenzoic acids), the

power of the acid decreases (Johnson, 1954b). Increasing the acid concentration from 1 to 10 mM corresponded to about a 10-fold increase in the amount of P released (Figure 6), suggesting that the strength of the acid was more important than the ability of the organic acids to complex metal in the release of elements from minerals (Manley and Evan, 1986). In many cases, the acids released more P from North Florida PR (medium reactive) than from Kodjari PR (low reactive), with the exception of sulfuric, nitric, hydrochloric and oxalic acids, which released more P from Kodjari than from North Florida PR. The effectiveness of oxalic acid in releasing P from Kodjari (5239 mg P kg^{-1} PR) was greater than that of sulfuric acid (4822 mg P kg^{-1} PR). The performance of tartaric acid in this case is remarkable (compare results obtained with 1 mM and 10 mM, Figures 5 and 6, respectively).

The amounts of P released from Kodjari and North Florida PRs were correlated with the amounts of Ca or Mg released by the various acids at equimolar concentration of 1 or 10 mM. Figure 7 shows that there is a positive correlation between P and Ca released on one hand and P and Mg released on the other hand, when the acids (1 mM) were equilibrated with Kodjari PR. The correlation was, however, stronger between P and Ca than between P and Mg, suggesting that most of the P released was Ca bound. The amounts of Ca released with oxalic acid were very low (<9 mmol kg^{-1}) and did not fit the quadratic model used to describe the relationship between P and Ca released. Increasing the concentration of the acids from 1 mM to 10 mM shifted the relationship between P and Ca (from a quadratic relationship to a linear) as well as the relationship

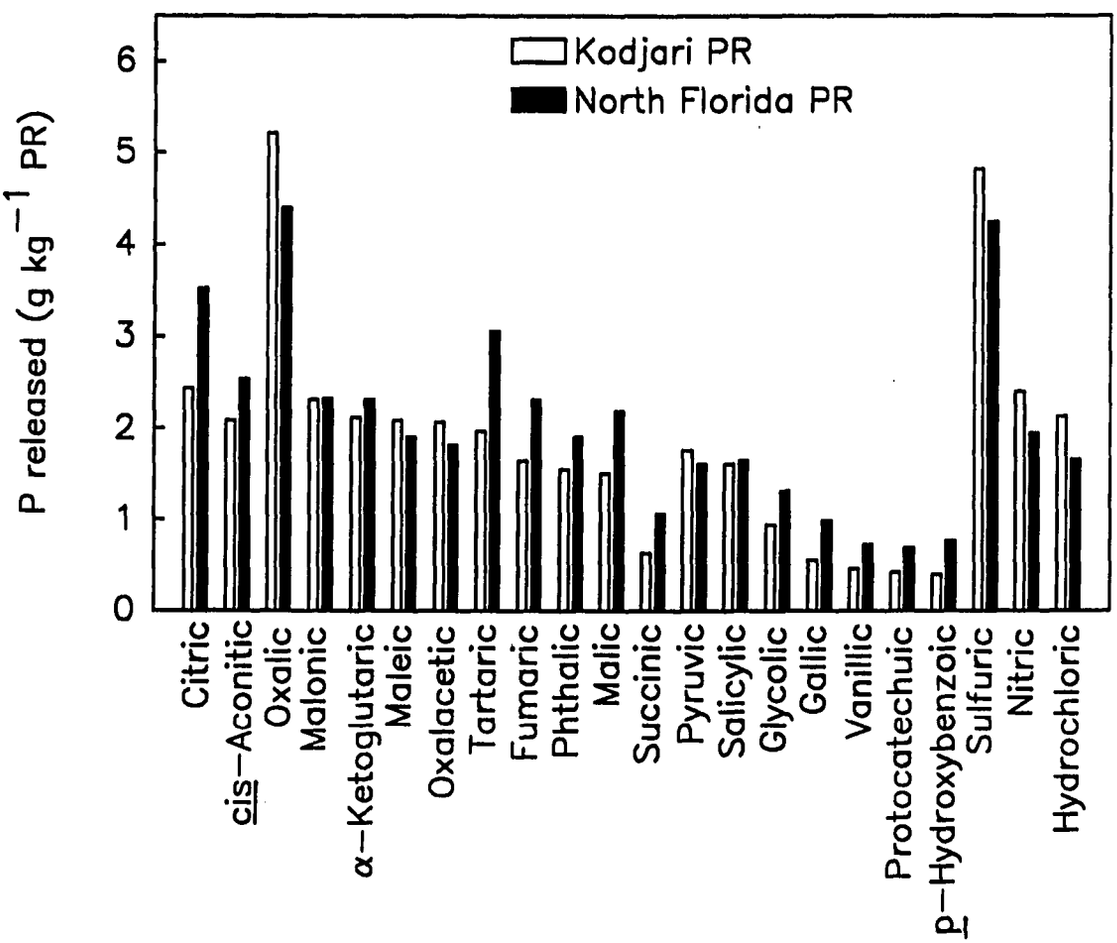


Figure 6. Effect of 10 mM organic or mineral acids on the release of phosphorus from Kodjari and North Florida phosphate rocks

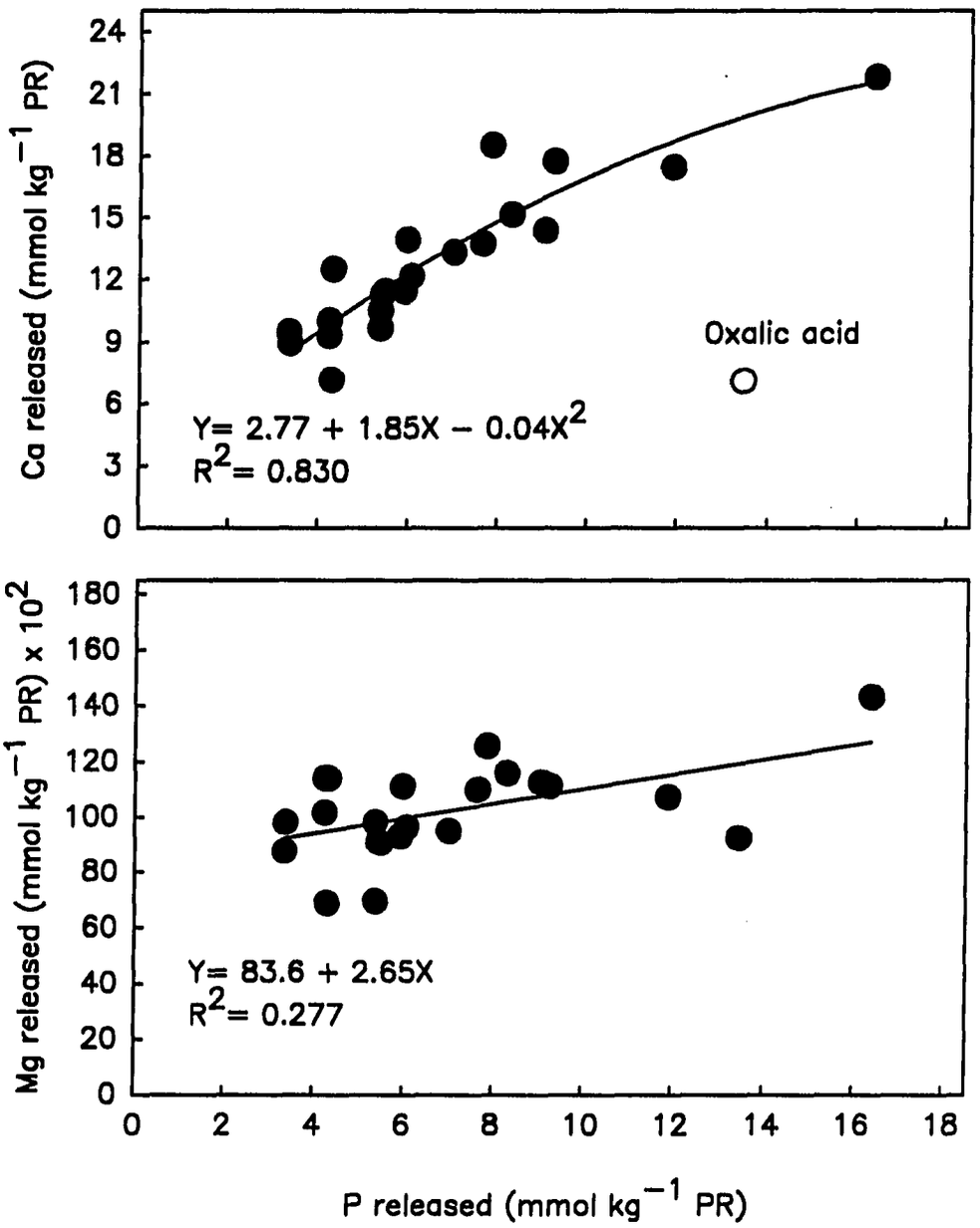


Figure 7. Relationship between Ca or Mg and P extracted from Kodjari PR with 1 mM mineral or organic acids. The open symbol was not included in the regression

between P and Mg (from a linear relationship to a quadratic); the correlation in both cases was highly significant (Figure 8). The correlation between P and Mg released from North Florida PR with the organic acids at 1 mM concentration was not significant (Figure 9), whereas the correlation between P and Ca released with the acids at 10 mM concentration was highly significant (Figure 10), again suggesting that the strength of the organic acid used plays a major role in P and Ca release; at 10 mM, organic acid bind more Ca than at 1 mM, therefore, releasing more P. The results reported in Figures 7-9 represent the amounts of P, Ca, and Mg released with all the mineral and organic acids used (each point represents the average of duplicate obtained with each acid). The individual averages for each acid are summarized in the Appendix (Tables 25 and 26).

Effect of Free Carbonates Removal on Phosphate Release

Many sedimentary phosphate rocks contain a small, but significant, amount of alkaline-earth carbonates. These alkaline-earth carbonates are present as free carbonates in the rocks and depress P extraction. In laboratory experiments, the values obtained in P release tests may be conflicting, especially for PRs containing substantial amounts of free carbonates. Silverman et al. (1952) showed that free carbonate can be removed from PR by digesting the rock in triammonium citrate solution (pH 8.1 ± 0.1). X-ray diffraction patterns obtained by Chien (1972) before and after two successive digestions of PR samples in the triammonium citrate solution (pH 8.1 ± 0.1) provided

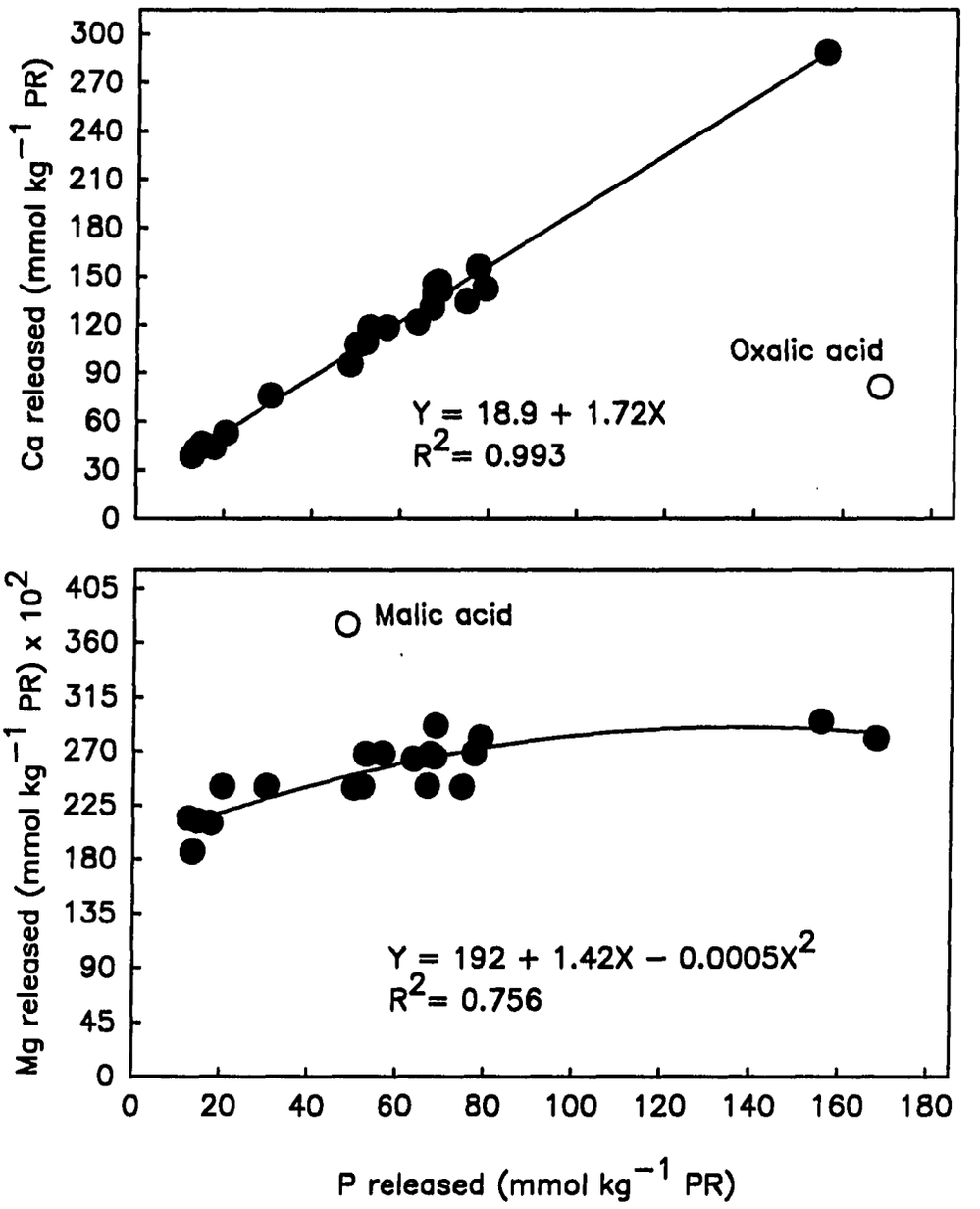


Figure 8. Relationship between Ca or Mg and P extracted from Kodjari PR with 10 mM mineral or organic acids. The open symbols were not included in the regression

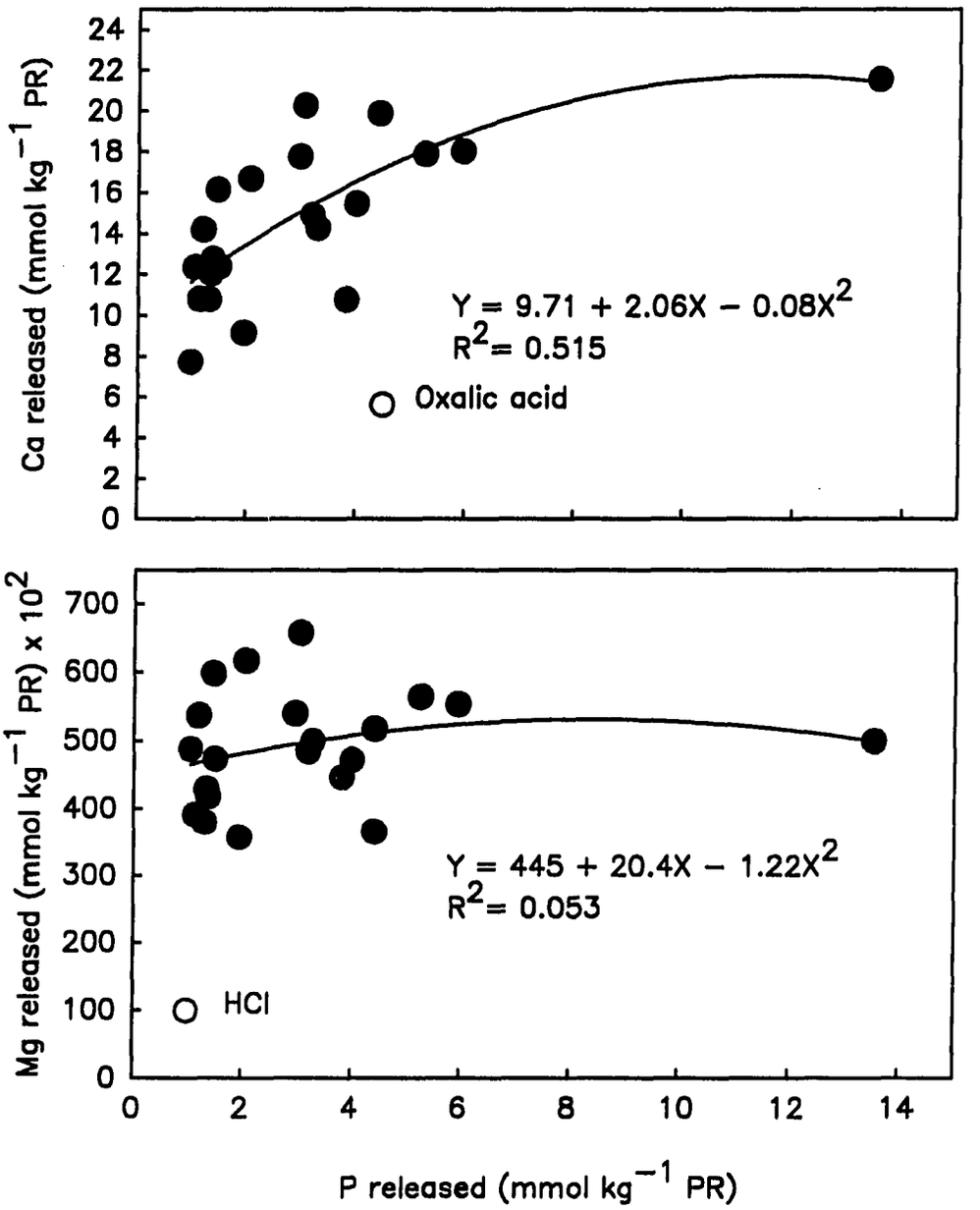


Figure 9. Relationship between Ca or Mg and P extracted from North Florida Pr with 1 mM mineral or organic acids. The open symbols were not included in the regression

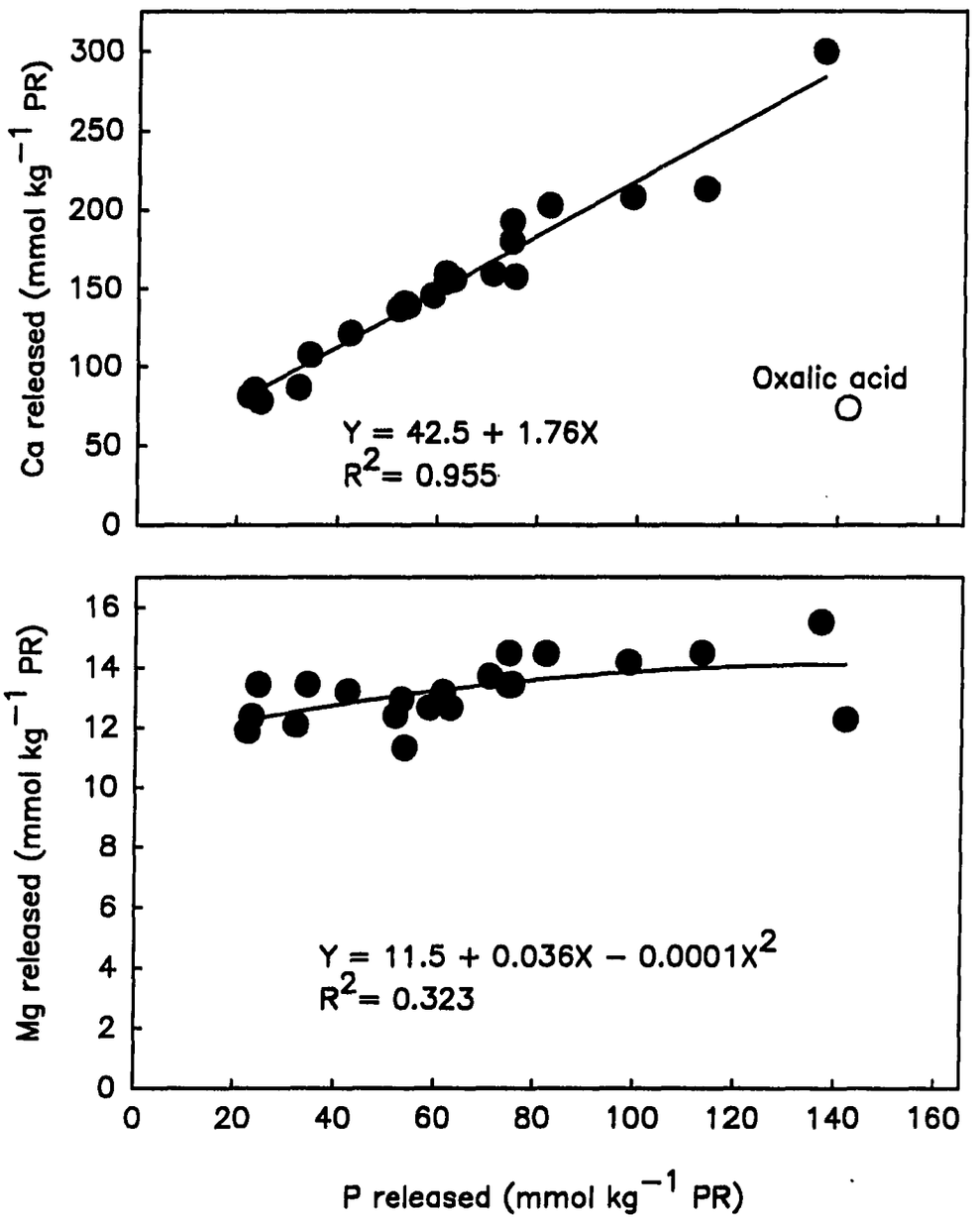


Figure 10. Relationship between Ca or Mg and P extracted from North Florida PR with 10 mM mineral or organic acids. The open symbol was not included in the regression

evidence of free carbonate removal. In this work, free carbonate was not completely removed from the PRs after two successive digestions. Evidence of this was provided by effervescence obtained after addition of a few drops of dilute HCl to samples before and after free carbonate removal. Moreover, comparison of the total C content of samples before and after free carbonate removal did not show the complete removal of free carbonate (Table 10). Further tests using x-ray diffraction patterns of North Florida PR before and after free carbonate removal showed the presence of calcite peaks at 3.04 Å (Figure 11). Thus, two successive digestions of PR with triammonium citrate does not ensure complete removal of free carbonate from PR. The effect of free carbonate removal on P released from 12 PR samples by equimolar concentration (10 mM) of 10 acids is illustrated in Figures 12-17. Almost all these figures show that all the acids used increased P release after free carbonate removal; the amounts of P released varied with type and structure of the acids as well as properties of the PR samples. Kodjari PR which is a low reactive PR contains only trace amounts of free $CaCO_3$; consequently, after removal of the free carbonate, the P released increased only slightly (Figure 12A) when oxalic, malonic, and citric acids were used. The P released by fumaric, salicylic, and cis-aconitic acids, however, increased substantially after carbonate removal (from 17 to 47 mmol; from 43 to 65 mmol; and from 53 to 83 mmol P kg^{-1}, respectively). The amounts of P released by oxalic and sulfuric acids are similar before and after carbonate removal. Large amounts of P were released by glycolic, pyruvic, fumaric, and sulfur acids after free carbonate removal from

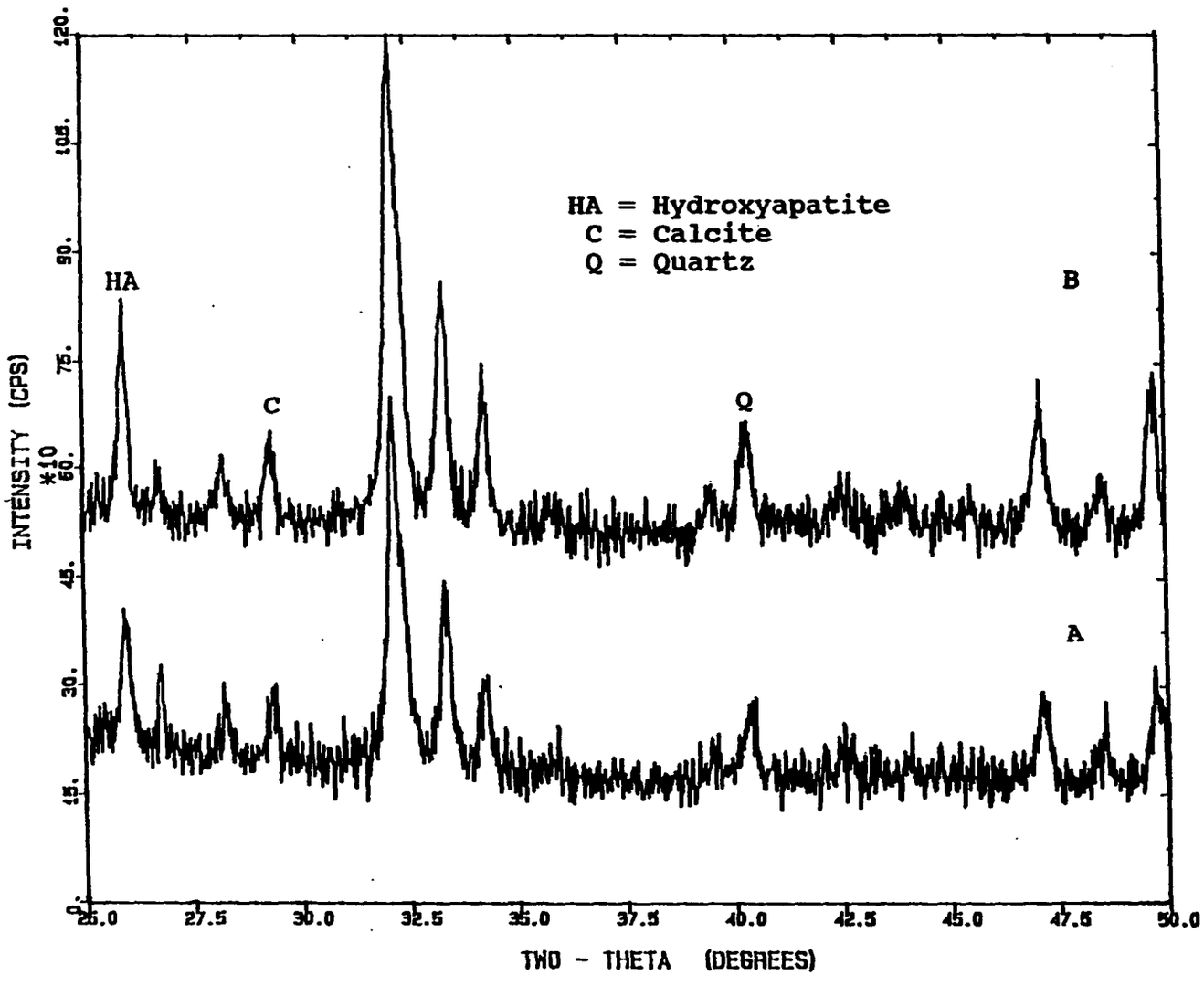
Table 10. Inorganic, organic, and total C contents and the effect of triammonium citrate extraction on C content of the phosphate rocks studied

Phosphate rock	Carbon[a]				
	Inorganic	Organic	Total	B[b]	A[b]
	%C				
Kodjari	0.18	0.19	0.36	0.27	0.30
Tahoua	0.14	0.17	0.31	0.21	0.30
North Carolina	1.03	1.94	2.98	2.96	3.08
Gafsa	1.24	0.68	1.92	2.34	2.20
Khourigba	0.54	0.32	0.86	1.25	1.41
Tilemsi Valley	0.36	0.22	0.59	0.66	0.92
Central Florida	0.57	0.43	1.00	0.98	1.14
Sechura	0.80	0.29	1.09	1.42	2.00
Minjingu	0.85	0.14	0.99	1.08	1.14
North Florida	0.53	0.39	0.92	1.22	1.39
Hahotoe	0.22	0.14	0.36	0.34	0.42
Parc W	0.16	0.09	0.26	0.32	0.26

[a]Inorganic C by the method of Bundy and Bremner (1972), Organic C by the method of Mebius (1962), and total C is the sum of inorganic and organic C.

[b]Total C by the Leco combustion method (Leco Model CHN 600 automatic analyzer). B, before, and A, after extraction with 0.5 M triammonium citrate (pH 8.1±0.1).

Figure 11. X-ray diffractions of the North Florida phosphate rock sample before (A) and after (B) extraction with triammonium citrate (0.5 M, pH 8.1). The peak at d-spacing of 3.04 Å corresponds to that of calcite


HA = Hydroxyapatite
C = Calcite
Q = Quartz
HA
C
Q
B
A
INTENSITY (CPS) *10
TWO - THETA (DEGREES)
0.
15.
30.
45.
60.
75.
90.
105.
120.
25.0
27.5
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47.5
50.0

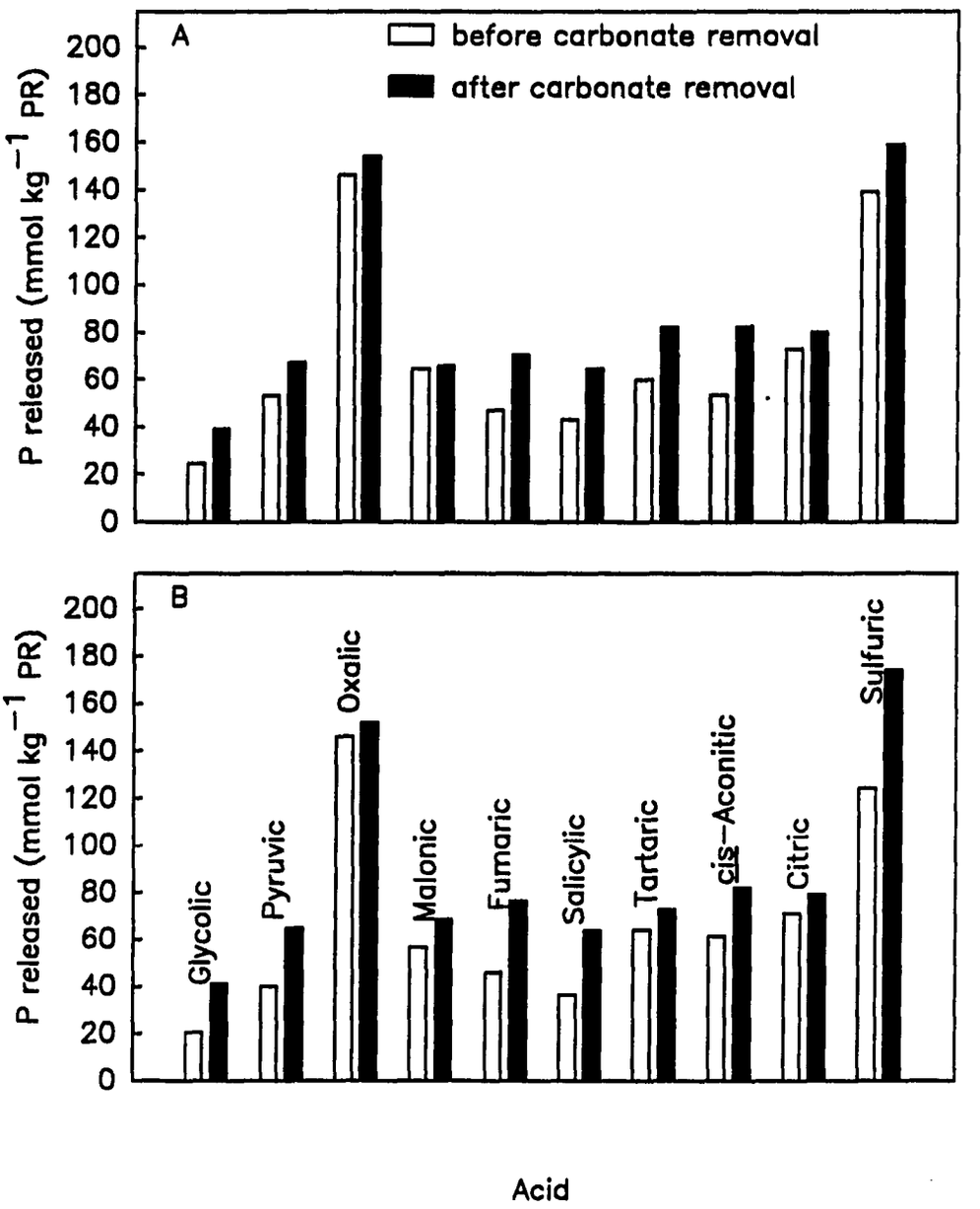


Figure 12. Effect of carbonate removal on the release of phosphorus from Kodjari (A) and Tahoua (B) phosphate rocks by 10 mM organic or sulfuric acid

Tahoua PR (Figure 12B). For Hahotoe PR, the amount of P released by oxalic and sulfuric acids decreased after free carbonate removal (Figure 13A), especially in the case of sulfuric acid. Presumably the P loss occurred during the extraction process with sulfuric acid and should not be interpreted as a loss which occurred during digestion of the rock with the triammonium citrate solution. Indeed, removal of free carbonate from PR by the alkaline triammonium citrate does not dissolve apatite (Smith and Lehr), 1966). When the acids were added to Parc W PR (low reactive PR), the amounts of P released reached 152 mmol P kg^{-1} before free carbonate removal and 163 mmol P kg^{-1} PR after free carbonate removal (Figure 13B) and the P release was greater with oxalic acid than with sulfuric acid. The largest increases in P release after free carbonate removal were associated with fumaric acid (44 mmol P kg^{-1} PR), cis-aconitic acid (42 mmol P kg^{-1} PR), salicylic and tartaric acids (35 mmol P kg^{-1} PR). Treatment of Parc W PR with citric acid did not result in large P release (Figure 13B). Khourigba PR is a medium reactive PR; before removal of free carbonate, glycolic, pyruvic, and salicylic acid were ineffective in releasing P from the rock (Figure 14A); malonic and fumaric acids on the other hand released only 6.7 mmol P kg^{-1} and 9.3 mmol P kg^{-1}, respectively. Removal of free carbonate from the rock, however, drastically increased the P release to 54 mmol P kg^{-1} with malonic acid and to 64.5 mmol P kg^{-1} with fumaric acid treatments. Considerable increase in the amounts of P released were also observed after equilibration of Khourigba PR with oxalic, tartaric, cis-aconitic, citric, and sulfuric acids following free carbonate removal; the percentage

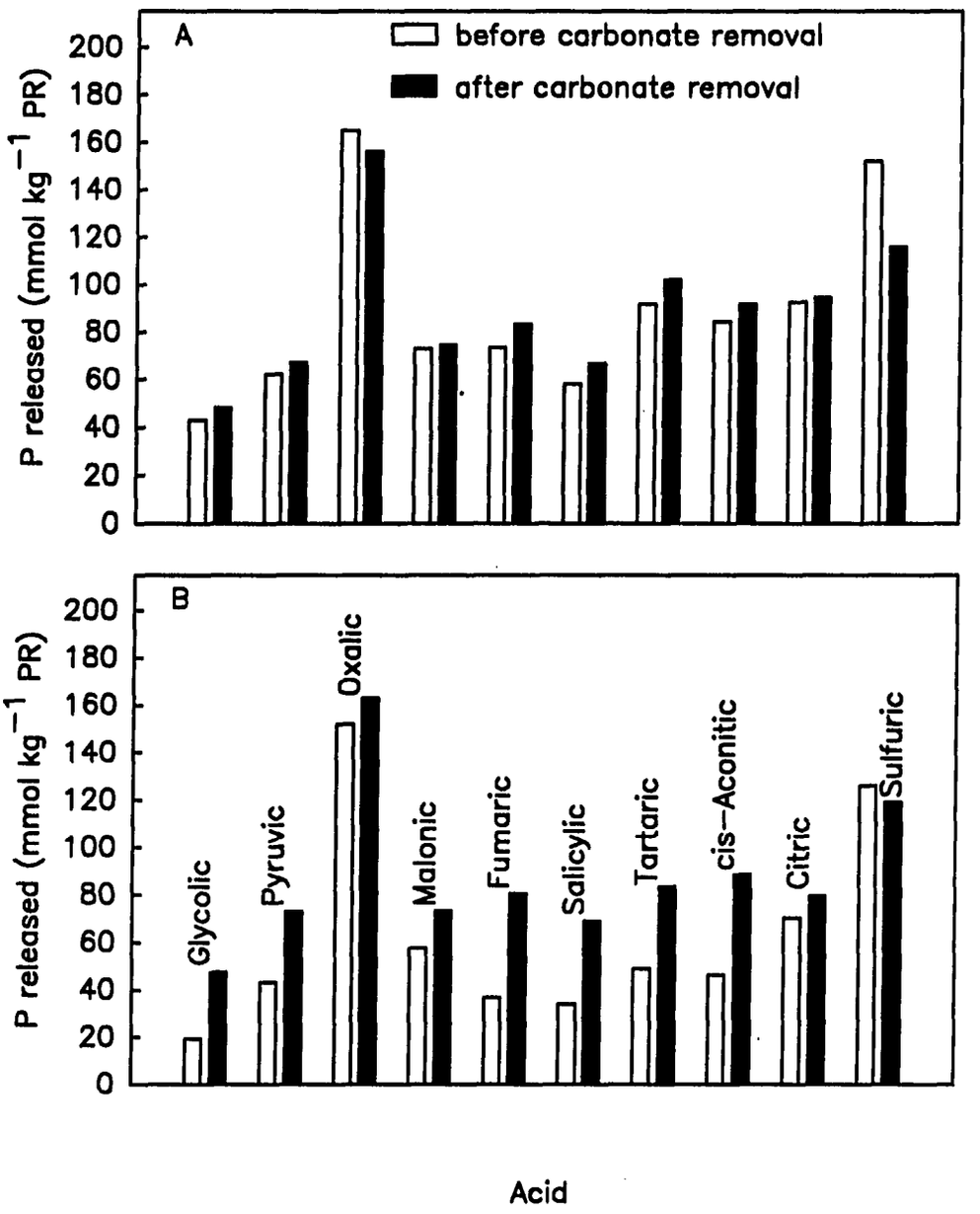


Figure 13. Effect of carbonate removal on the release of phosphorus from Hahotoe (A) and Parc W (B) phosphate rocks by 10 mM organic or sulfuric acid

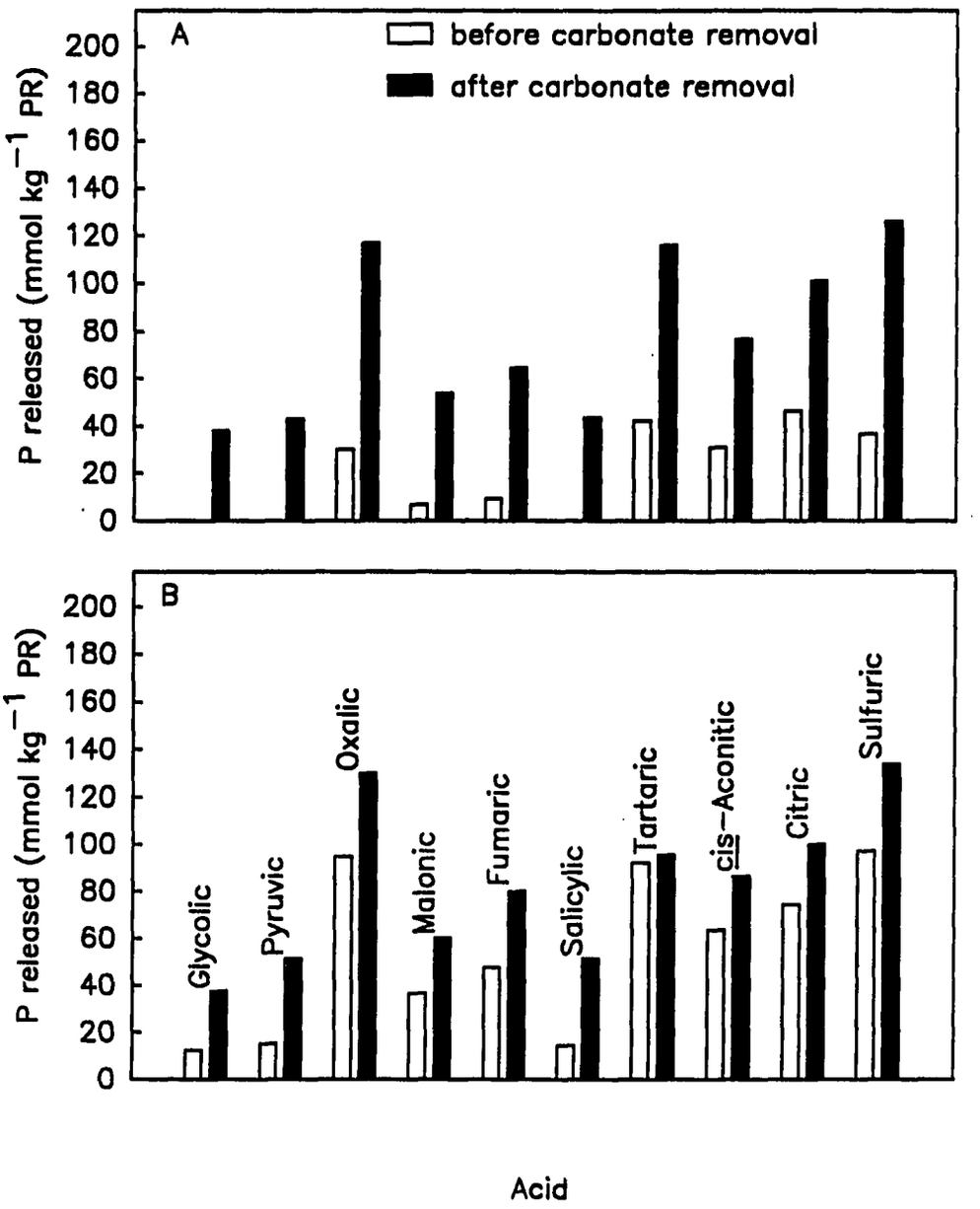


Figure 14. Effect of carbonate removal on the release of phosphorus from Khouribga (A) and Tilemsi (B) phosphate rocks by 10 mM organic or sulfuric acid

increase in P release was estimated to 387, 275, 248, 218, and 343%, respectively. The five most effective acids after free carbonate removal were: sulfuric, oxalic, and tartaric (both dicarboxylic acids), and citric and cis-aconitic (both tricarboxylic acids) (Figure 14A). A different picture, however, was observed when Tilemsi Valley PR (medium reactive PR) was equilibrated with the acids (Figure 14B). Glycolic, pyruvic, and salicylic acids released P from the rock before free carbonate removal and the sharp increase in P released by oxalic, tartaric, cis-aconitic, and sulfuric acids after free carbonate removal did not occur (Figure 14B). Again oxalic acid was almost as effective as sulfuric acid. Removal of free carbonate from Central Florida PR (medium reactive PR) did not increase P release greatly (Figure 15A); some increases, however, may be pointed out: 14.4, 15.1, and 18 mmol P kg^{-1} with pyruvic, fumaric, and salicylic acids, respectively. Dicarboxylic (oxalic and tartaric acids), citric and sulfuric acids were the most effective in releasing P from North Florida PR before and after free carbonate removal (Figure 15B), whereas the monocarboxylic (glycolic and pyruvic) and the aromatic (salicylic) acids were the least effective. After removal of free carbonate from North Florida PR, the P release increased form 94.5 to 129 mmol P kg^{-1} with tartaric acid (Figure 15B).

The most interesting results were those obtained with the high reactive PRs (North Carolina, Gafsa, Minjingu, and Sechura PRs). Figures 16 and 17 illustrate the need to remove free carbonate from PR samples before dissolution tests (Van Kauwenbergh and McClellan, 1990). The monocarboxylic acids were not effective in releasing

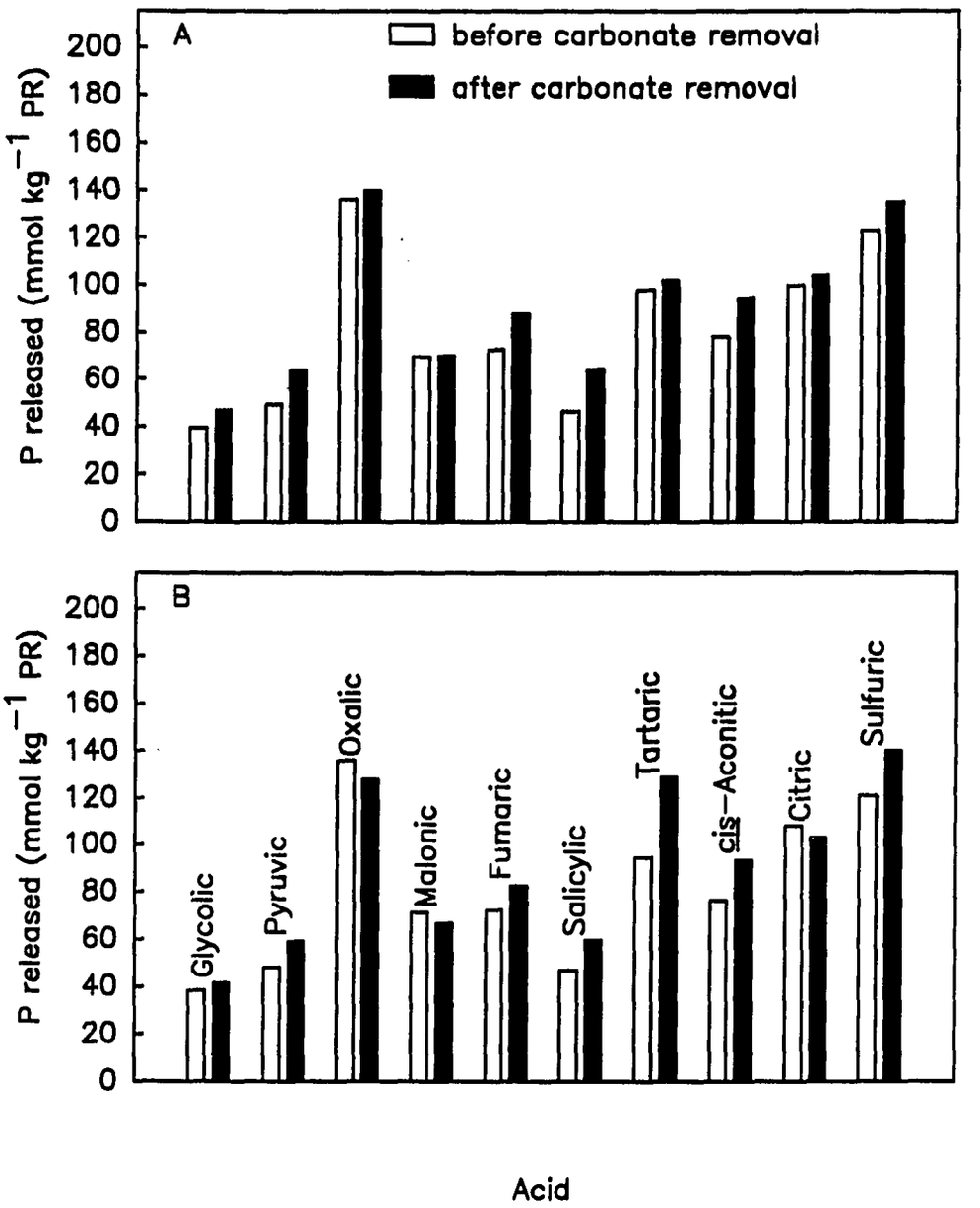


Figure 15. Effect of carbonate removal on the release of phosphorus from Central Florida (A) and North Florida (B) phosphate rocks by 10 mM organic or sulfuric acid

P from North Carolina PR before free carbonate removal (Figure 16A); the most effective acid was citric acid which released 48.4 mmol P kg^{-1} more than the un-washed sample. Removal of free carbonate, however, considerably increased the P release, which reached to 90, 83, 71, 98, and 98 mmol P kg^{-1} when oxalic, tartaric, cis-aconitic, citric,and sulfuric acids were used, respectively. The largest increase in P released after free carbonate removal was observed for the oxalic acid treatment (75.4 mmol P kg^{-1}) (Figure 16A). A similar picture was observed for the Gafsa PR in which case the P released was not more than 83 mmol P kg^{-1} (Figure 16B). Surprisingly, oxalic and sulfuric acids were not powerful enough to release P from Gafsa PR without free carbonate removal; 3.4 and 4.3 mmol P kg^{-1} released, respectively. In the case of Minjingu PR (Figure 17A), not only glycolic, pyruvic, amonic, fumaric, salicylic and sulfuric acid treatments did not release P before free carbonate removal but also oxalic, tartaric and cis-aconitic acid treatments did not release substantial amounts of P either (only trace amounts were released). For Sechura PR (Figure 17B), the P release by glycolic, pyruvic, and salicylic acids before free carbonate removal was depressed; the washing of the rock with triammonium citrate, however, improved the P release; 33.5 mmol P kg^{-1} with glycolic and 38 mmol P kg^{-1} with pyruvic acid. Washing also increased the P release from the Sechura PR from 21.4 to 111 mmol P kg^{-1} with oxalic acid, from 36 to 102 mmol P kg^{-1} with tartaric acid, from 28.7 to 85.9 mmol P kg^{-1} with cis-aconitic acid, from 67 to 112 mmol P kg^{-1} with citric acid, and from 26.2 to 112 mmol P kg^{-1} with sulfuric acid treatments (Figure 17B).

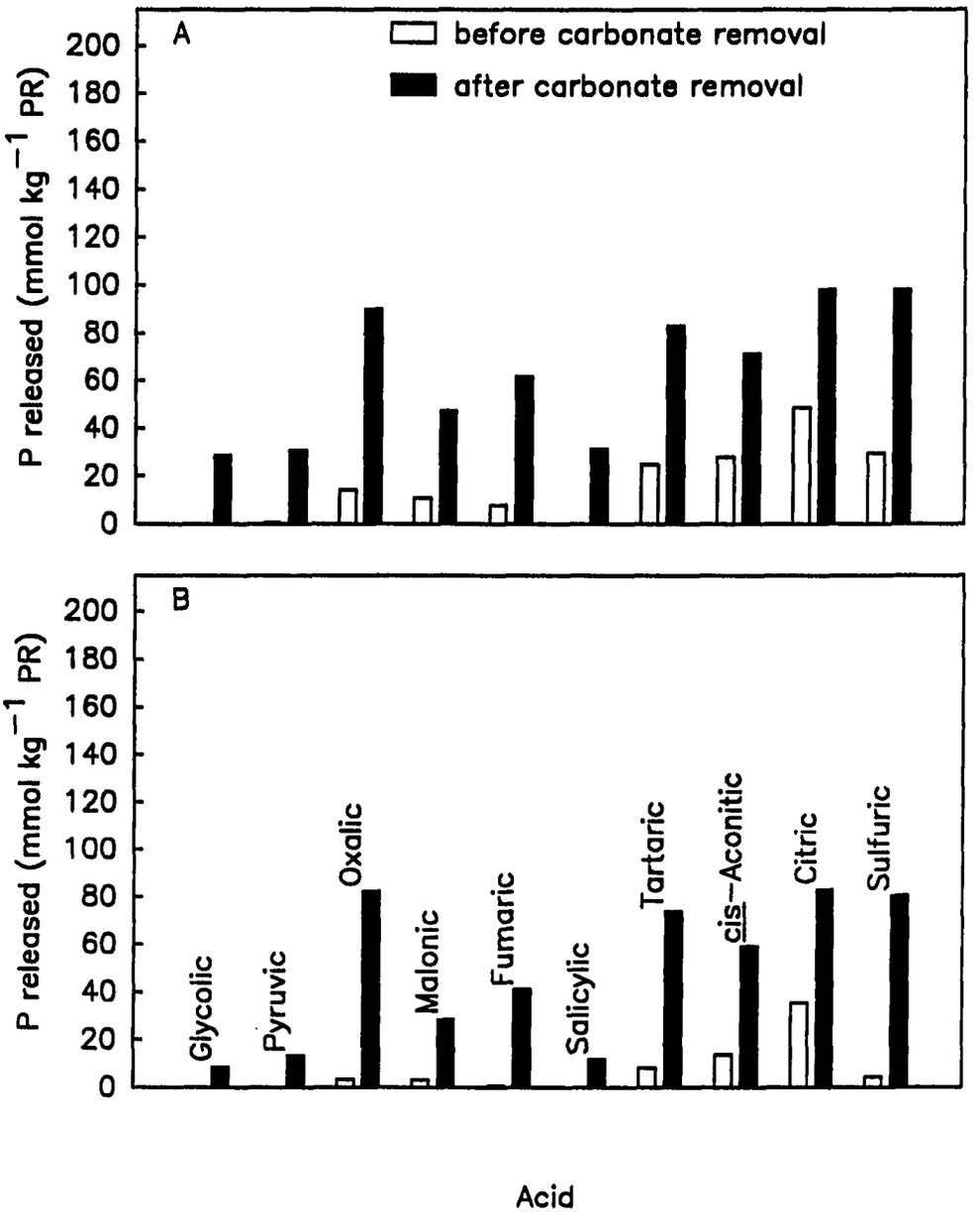


Figure 16. Effect of carbonate removal on the release of phosphorus from North Carolina (A) and Gafsa (B) phosphate rocks by 10 mM organic or sulfuric acid

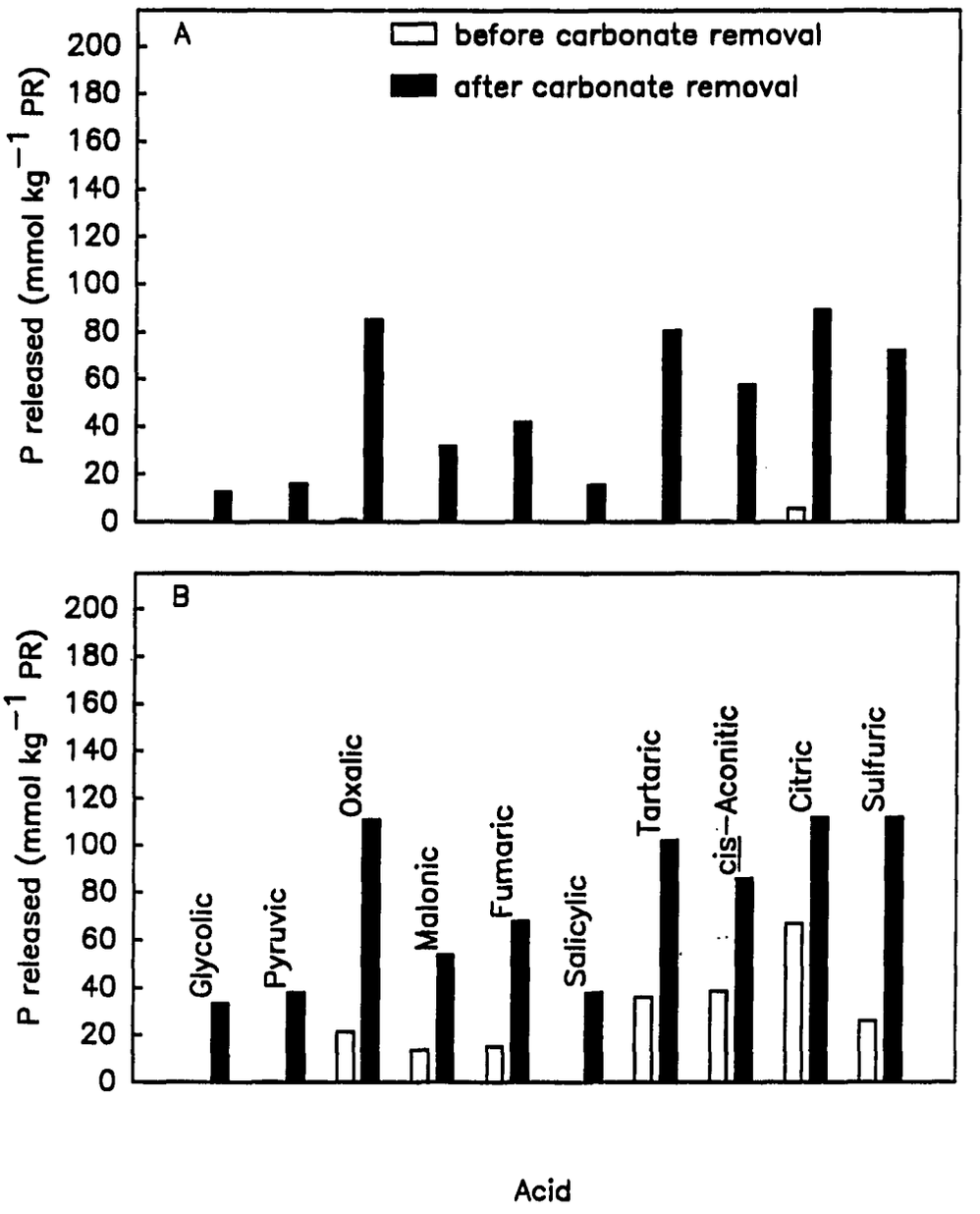


Figure 17. Effect of carbonate removal on the release of phosphorus from Minjingu (A) and Sechura (B) phosphate rocks by 10 mM organic or sulfuric acid

These results suggest that the presence of free carbonate, even in very small amounts in PRs, considerably depresses P solubility; increase in the P release can be achieved only by removing the free carbonate. Clark (1955) pointed out that he could not obtain a solubility-product constant for hydroxyapatite in the presence of atmospheric carbon dioxide. Moreover, Braithwaite et al. (1989) showed a suppression of P solubility due to common ion effect observed after addition of calcium chloride, calcium sulfate, and calcium phosphate. Furthermore, they stressed that P solubility was severely depressed by addition of calcium carbonate and sodium carbonate due to reaction with acidic extractants. Throughout this discussion, it was demonstrated that not only the P release varied considerably before and after free carbonate removal, but also that the amounts of P released varied among acids and among PR samples. The general tendency was that the amounts of P released from low reactive PRs (Kodjari, Tahoua, Hahotoe, and Parc W) were greater than those released from medium reactive PRs (Khourigba, Tilemsi Valley, North Florida, and Central Florida), and the amounts of P released from the latter group were greater than those released from the high reactive PRs (North Carolina, Gafsa, Sechura, and Minjingu). This is true even after the carbonate removal.

Although the triammonium citrate solution was not effective in removing all the free carbonate from the rocks, as evident from the various tests performed on samples before and after two successive digestions, treatment of the rocks with triammonium citrate solution changed perhaps physical (surface area) and chemical properties of the

rocks. Table 11 shows that digestion of PRs with triammonium citrate altered the Ca/P ratios. With a few exceptions, the ratio decreased after washing, suggesting that some Ca was washed out from the rock after the triammonium citrate treatment. I tried to investigate the possible reasons that may cause greater P release from low reactive PRs.

Inorganic P released from PRs with low-molecular-weight organic acids is a result of an acidic effect caused by the dissociation of protons of the organic acids in the PR-solution mixture, or a result of a formation of stable-organo-metallic complexes implicating metal cations which are associated with P in the PR sample, or from a combination of the two. Even though the composition of sedimentary apatites has been described by the Ca, Na, Mg, P, CO_2, and F contents, a few samples contained small, but significant amounts of Al in the form of aluminum phosphates; most samples contained small amounts of Mg, Ba, and Sr which can substitute for Ca in the apatite structure (Smith and Lehr, 1966). Although these metals (Al, Fe, Mg, Ba, Sr) are found in small amounts associated with P in the rock, the effectiveness of any organic acid to complex these metals will undoubtedly contribute to a greater P release from the rock. Thus, it is of interest to test for Al and Fe release from low, medium, and high reactive PRs before carbonate removal by each individual acid. Figure 18 illustrates that large amounts of Al and Fe were released by the acids studied. The acids were especially effective in releasing the metals from Kodjari PR and Parc W PR; up to 21.2 mmol Al kg^{-1} was released with citric acid from Kodjari PR. Other

Table 11. Mole ratios of calcium and phosphorus released from phosphate rocks by organic or sulfuric acid (10 mM) before and after carbonate removal with triammonium citrate

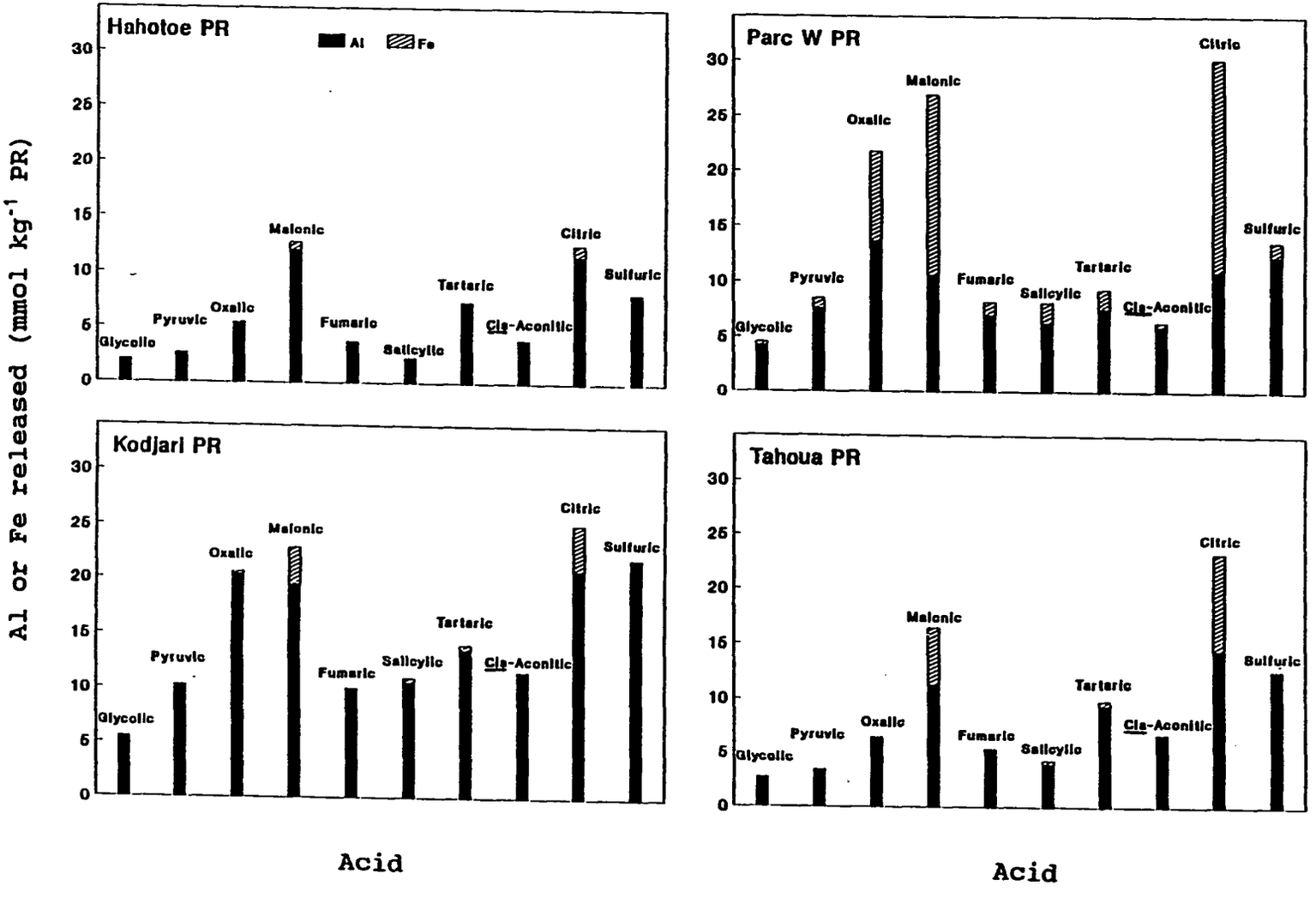
	Mole ratio of Ca and P released by the acid specified									
	Glycolic[a]		Pyruvic		Oxalic		Malonic		Fumaric	
PR	A	B	A	B	A	B	A	B	A	B
Kodjari	2.43	1.28	2.26	1.47	0.50	0.43	2.07	1.80	2.18	2.08
Tahoua	4.09	0.60	2.90	1.28	0.54	0.48	2.73	1.77	3.48	1.92
North Carolina	844	2.56	2.55	0.43	255	0.43	19.5	2.68	36.3	3.16
Gafsa	-	7.76	-	5.40	15.3	0.24	76.7	3.94	324	4.14
Khourigba	-	1.65	11300	2.16	0.56	0.51	22.4	2.70	23.7	2.81
Tilemsi Valley	8.56	1.39	7.38	1.42	0.60	0.35	4.08	1.94	4.75	2.04
Central Florida	3.02	1.98	2.84	1.84	0.59	0.51	2.42	2.18	3.03	2.15
Sechura	2133	2.59	554	2.13	3.09	0.43	14.4	2.59	17.8	2.83
Minjingu	-	4.00	-	2.91	14.7	0.18	-	2.56	-	3.50
North Florida	2.99	3.04	2.91	1.64	0.58	0.49	2.32	2.13	2.85	2.36
Hahotoe	2.32	1.36	2.31	1.23	0.58	0.55	2.25	2.00	2.55	2.20
Parc W	2.65	1.92	2.37	1.52	0.58	0.59	2.27	1.96	2.74	2.06

[a]-indicates no P release before carbonate removal. A before and B after carbonate removal with 0.5 M triammonium citrate.

Table 11. Continued

	Mole ratio of Ca and P released by the acid specified									
	Salicylic		Tartaric		Cis-aconitic		Citric		Sulfuric	
PR	A	B	A	B	A	B	A	B	A	B
Kodjari	2.15	1.68	2.19	1.80	2.12	1.85	1.98	1.68	2.22	1.11
Tahoua	2.89	1.67	2.38	2.00	2.54	1.88	2.08	1.59	2.48	1.31
North Carolina	2100	3.12	3.24	1.14	9.46	0.28	6.55	2.22	8.68	1.91
Gafsa	-	6.86	11.3	0.79	19.6	3.20	8.98	2.73	60.8	1.73
Khourigba	-	2.89	1.66	0.93	6.47	2.66	4.09	1.88	6.40	1.36
Tilemsi Valley	7.19	1.88	1.08	1.76	2.99	1.84	2.46	1.61	2.81	1.33
Central Florida	2.67	2.15	1.35	1.87	2.40	2.10	2.10	1.71	2.62	1.95
Sechura	-	2.74	3.75	1.83	5.61	2.26	4.12	1.84	10.4	2.04
Minjingu	-	3.92	138	0.90	1.77	2.61	44.9	1.62	0	1.73
North Florida	2.64	2.14	1.67	0.85	2.47	2.07	1.99	1.90	2.63	1.51
Hahotoe	2.22	1.78	1.92	1.70	2.06	1.94	1.94	1.92	2.22	2.97
Parc W	2.40	2.03	2.25	1.81	2.14	1.82	1.71	1.77	2.25	1.26

Figure 18. Effect of 10 mM organic or sulfuric acid on the release of Al and Fe from low reactive phosphate rocks


Hahotoe PR
Al
Fe
Parc W PR
Kodjari PR
Tahoua PR
Al or Fe released (mmol kg-1 PR)
Glycolic
Pyruvic
Oxalic
Malonic
Fumaric
Salicylic
Tartaric
Cis-Aconitic
Citric
Sulfuric
Acid
Acid

acids, oxalic, malonic, tartaric, and cis-aconitic released, respectively, 20.4, 19.5, 13.6, and 11.6 mmol Al kg^{-1} from the same Kodjari PR (Figure 18). Three organic acids appeared to be the most effective in releasing Fe from Parc W PR: citric acid (19.2 mmol Fe kg^{-1}), malonic acid (16.3 mmol Fe kg^{-1}), and oxalic acid (8.2 mmol Fe kg^{-1}). In general, more Al was released with the acids than Fe from Hahotoe, Kodjori, and Tahoua PRs.

The amounts of Al and Fe released from the medium reactive PRs are shown in Figure 19. Note the small amounts of Al and Fe released from Khourigba and Tilemsi Valley PRs by any of the acids and the absence of P release with glycolic, pyruvic, oxalic, salicylic, tartaric, and cis-aconitic acids. Substantial amounts of Al were released, however, from Central Florida and North Florida PRs. Malonic, tartaric, and citric acids appeared to be the most effective in releasing Al from central Florida and North Florida Prs. Very small amounts of Al or Fe were released from the high reactive PRs (Figure 20), presumably because in these high reactive PRs there is no Al or Fe associated with P in the apatite structure; the same thing is true for some medium reactive phosphate rocks such as Khourigba and Tilemsi Valley Prs, which perhaps contain only a very small portion of P associated with these metals. It is known that the greater the affinity of an organic acid for a metal cation, the stronger its ability to form a stable organo-metallic-complex. Bruckert (1970) stated that citric acid and oxalic acid solubilize large amounts of Al and Fe; citric acid, however, quantitatively complexes more Fe than oxalic acid. Some organic acids such as oxalic,

Figure 19. **Effect of 10 mM organic or sulfuric acid on the release of Al and Fe from medium reactive phosphate rocks**

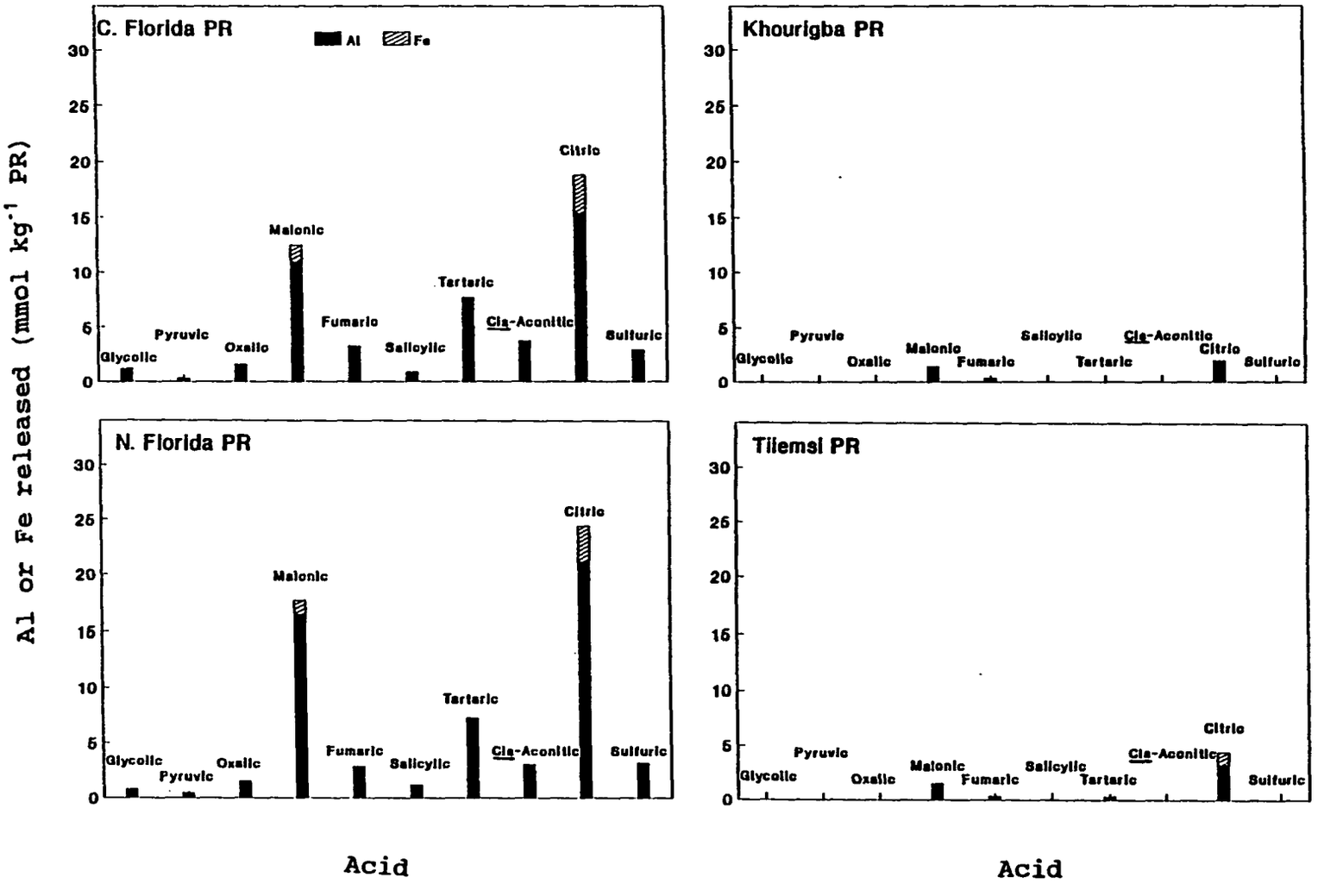
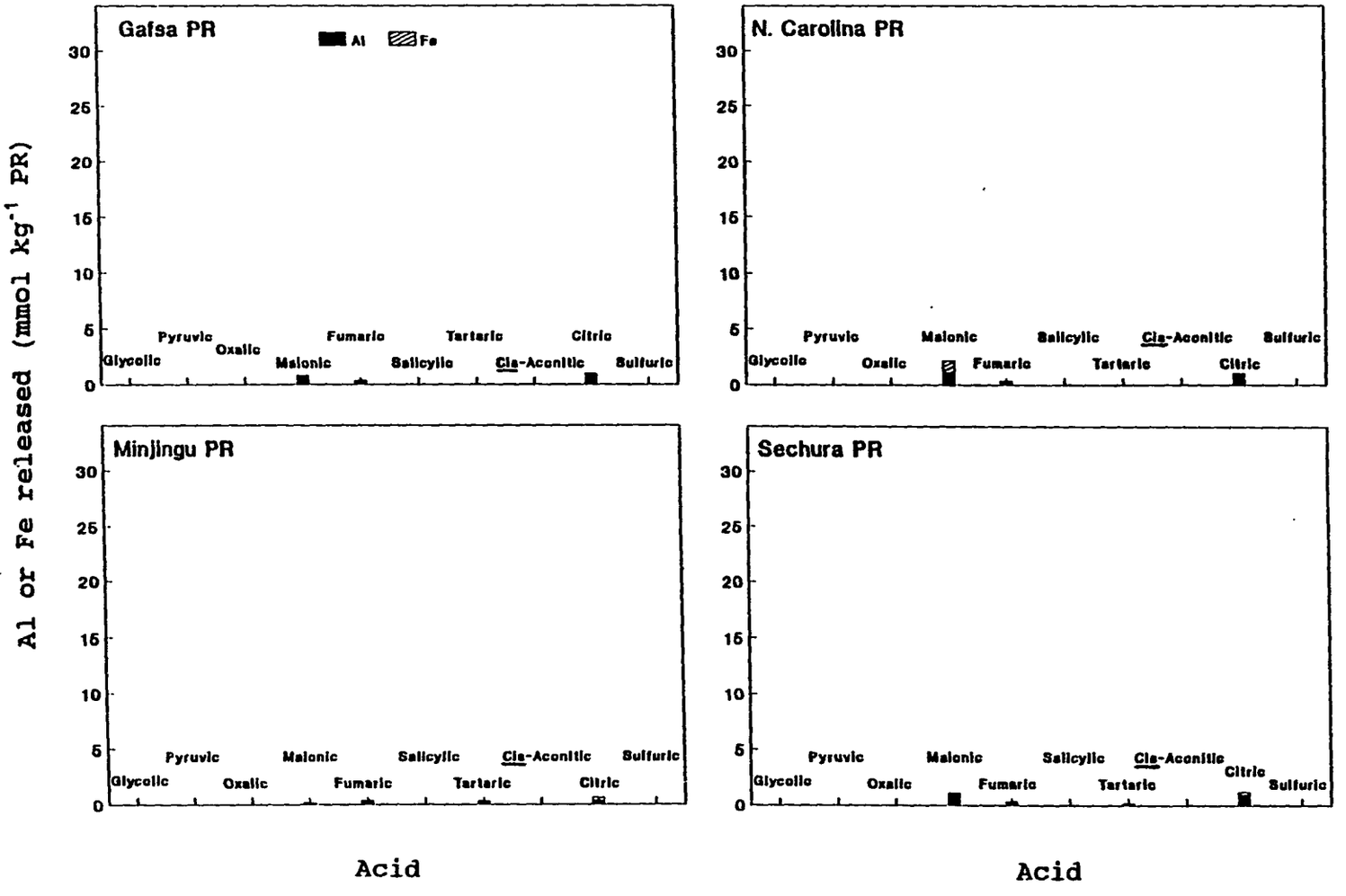

C. Florida PR
Al
Fe
Khourigba PR
N. Florida PR
Tilemsi PR
Al or Fe released (mmol kg-1 PR)
Glycolic
Pyruvic
Oxalic
Malonic
Fumaric
Salicylic
Tartaric
Cis-Aconitic
Citric
Sulfuric
Acid
0
5
10
15
20
25
30

Figure 20. Effect of 10 mM organic or sulfuric acid on the release of Al and Fe from high reactive phosphate rocks


Gafsa PR
Al
Fe
N. Carolina PR
Minjingu PR
Sechura PR
Al or Fe released (mmol kg-1 PR)
30
25
20
15
10
5
0
Glycolic
Pyruvic
Oxalic
Malonic
Fumaric
Salicylic
Tartaric
Cis-Aconitic
Citric
Sulfuric
Acid

tartaric, malonic, and citric acids have the ability to form five- or six-membered chelating rings that are considered to be very stable. Therefore, the ability of these organic acids to complex metals, especially Ca, Al, and Fe appeared to be the dominant factor in the P released. Fox et al. (1990) found an exponential relationship between Al and inorganic P released.

Phosphorus in apatite may be associated with Ca, Mg, Al, or Fe. Figures 21-26 show the relationship between the amounts of P and Ca released by equimolar concentration (10 mM) of 10 acids, before and after free carbonate removal. These figures show that removal of free carbonates from the rocks increased P release and improved the regression coefficients. The amounts of Ca, Mg, Al, Fe, and P release with the individual acid are summarized in the Appendix (Tables 27 and 28).

The amounts of P and Ca released from Kodjari PR were significantly correlated before and after free carbonate removal ($p < 0.001$) (Figure 21). The values obtained with sulfuric and oxalic acids did not fit the relationship. Similar results were obtained for Tahoua PR (Figure 21). A quadratic model was used to describe the relationship between P and Ca for North Carolina (Figure 22); the correlation was significant ($p < 0.001$). The values of the acids that did not fit the relationship were for fumaric, tartaric, and oxalic acids. For Gafsa PR, a quadratic model was adequate to describe P and Ca relationship before free carbonate removal, whereas a linear model was appropriate after free carbonate removal (Figure 22). The correlation was significant before ($p < 0.01$) and after ($p < 0.001$) removal of free carbonate. The values obtained with oxalic, tartaric, sulfuric,and fumaric acids did not, however, fit the relationships established between P and Ca (Figure 22).

The amounts of P and Ca released from Khourigba PR were significantly correlated before ($r = 0.912^{***}$) and after ($r = 0.962^{***}$) carbonate removal (Figure 23). The values obtained with tartaric and oxalic acid deviated from this relationship.

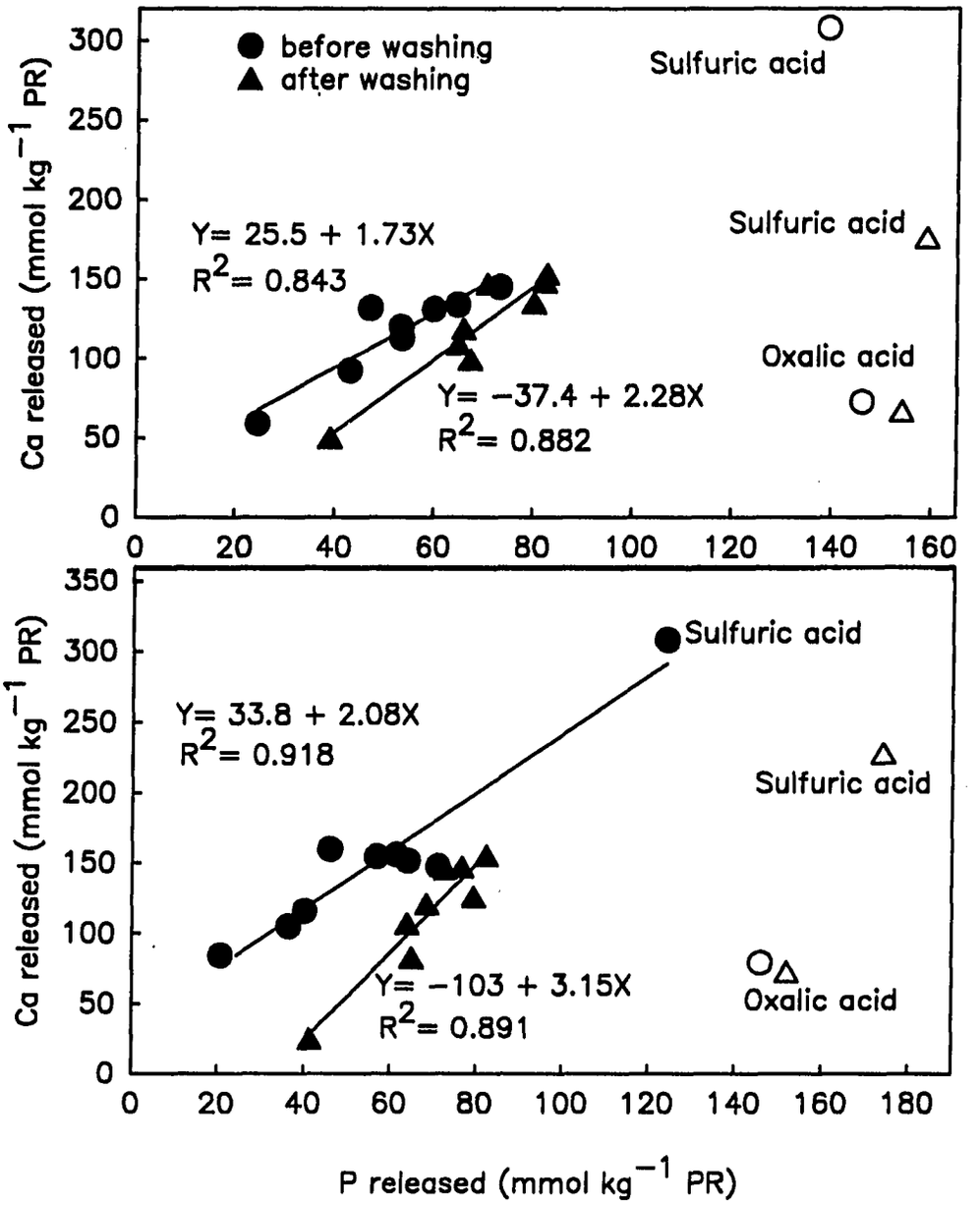


Figure 21. Relationships between Ca and P released from Kodjari (top) and Tahoua (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression.

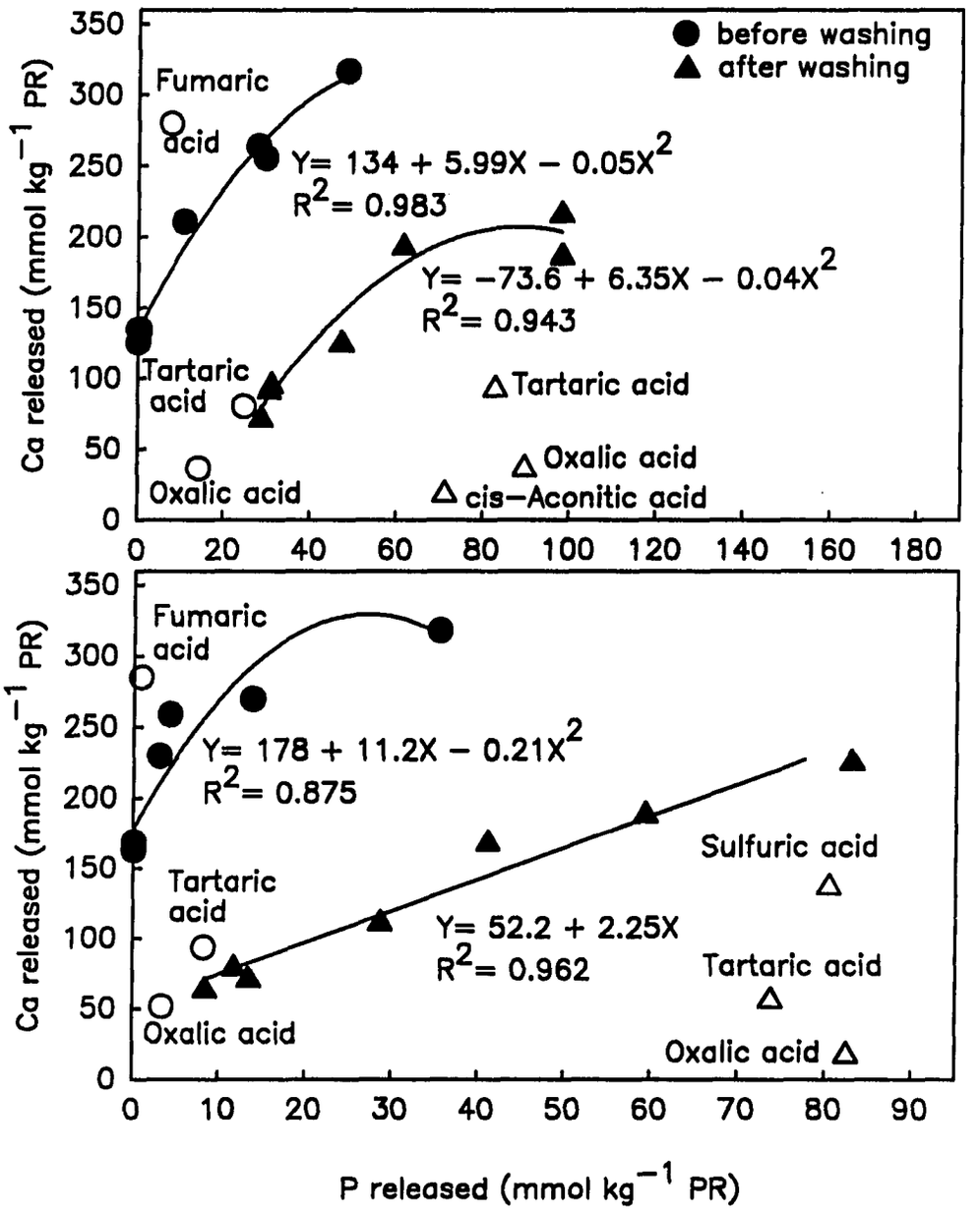


Figure 22. Relationships between Ca and P released from North Carolina (top) and Gafsa (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

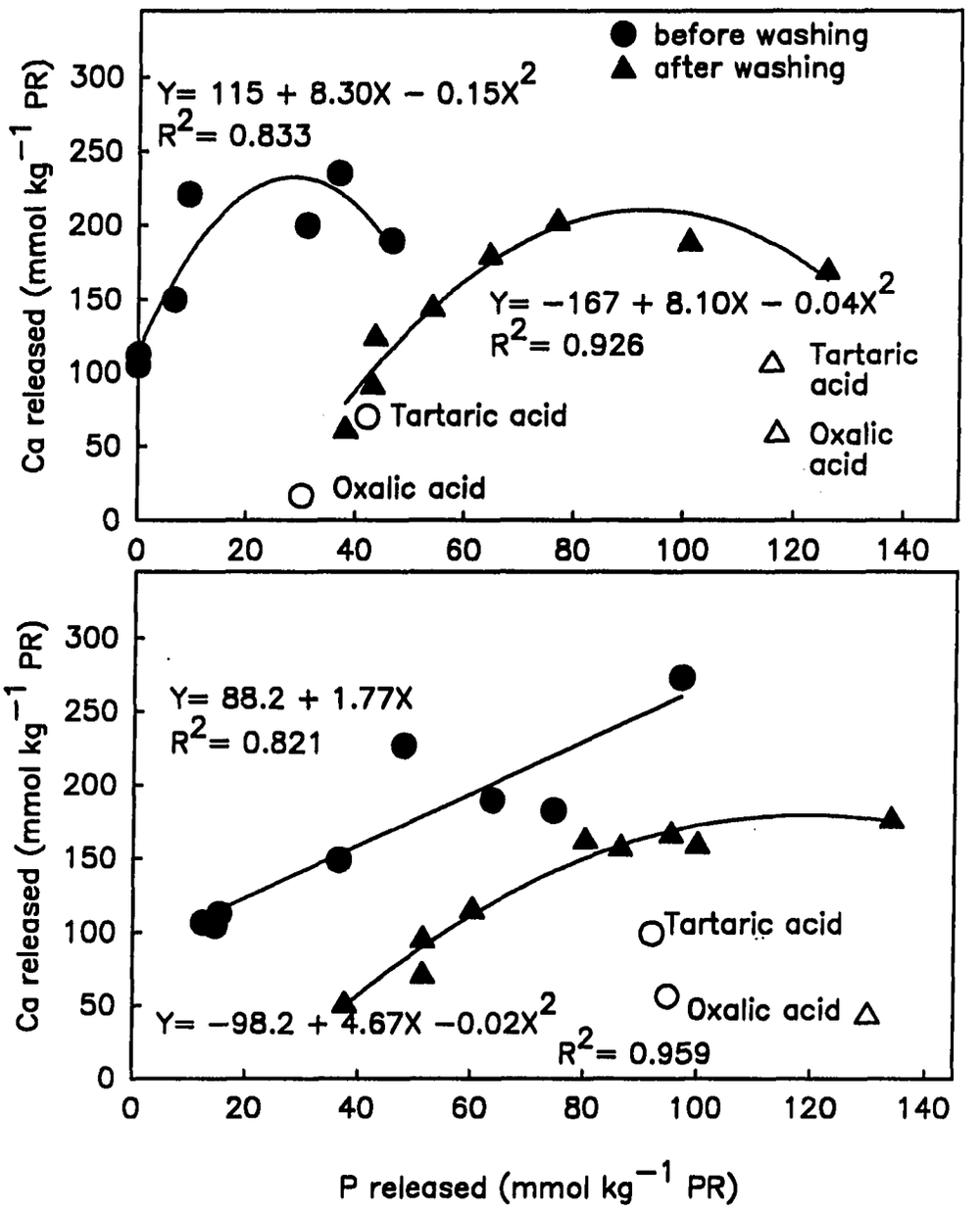


Figure 23. Relationships between Ca and P released from Khourigba (top) and Tilemsi Valley (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affect by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

After removal of free carbonate from Tilemsi Valley PR (Figure 23), the linear relationship between Ca and P shifted to a quadratic relationship and the regression coefficient improved from 0.821 to 0.959.

For Central Florida PR (Figure 24), the correlation was significant ($p < 0.001$) both before and after free carbonate removal; but still the values obtained with tartaric and oxalic acids did not fit the relationship. Free carbonate removal greatly improved the regression coefficient from 0.756 to 0.936 for Sechura PR (Figure 24).

The effect of free carbonate removal is best illustrated on Figure 25, where the removal of free carbonate brought the data points closer to the line (for Minjingu PR). The results reported in Figures 25 and 26 for North Florida PR and Hahotoe PR, respectively, the removal of free carbonate failed to improve the correlation between P and Ca. Figure 26 shows a high regression coefficient between P and Ca before (R^2 = 0.947) and after free carbonate removal from Parc W PR (R^2 = 0.785). In all cases, oxalic acid and, in many cases, tartaric acid did not fit the relationships because of the relatively low Ca that these acids released into solution.

The relationships between P and Mg released from the PRs by the acids are shown in Figures 27-32. Even though the amounts of Mg released were relatively low (<42 mmol Mg kg^{-1}), and varied widely among the phosphate rocks (as high as 41 - mmol Mg kg^{-1} for Gafsa PR before free carbonate removal to as low as 0.2 mmol kg^{-1} for Kodjari and Tahoua PR after free carbonate removal), it was significantly

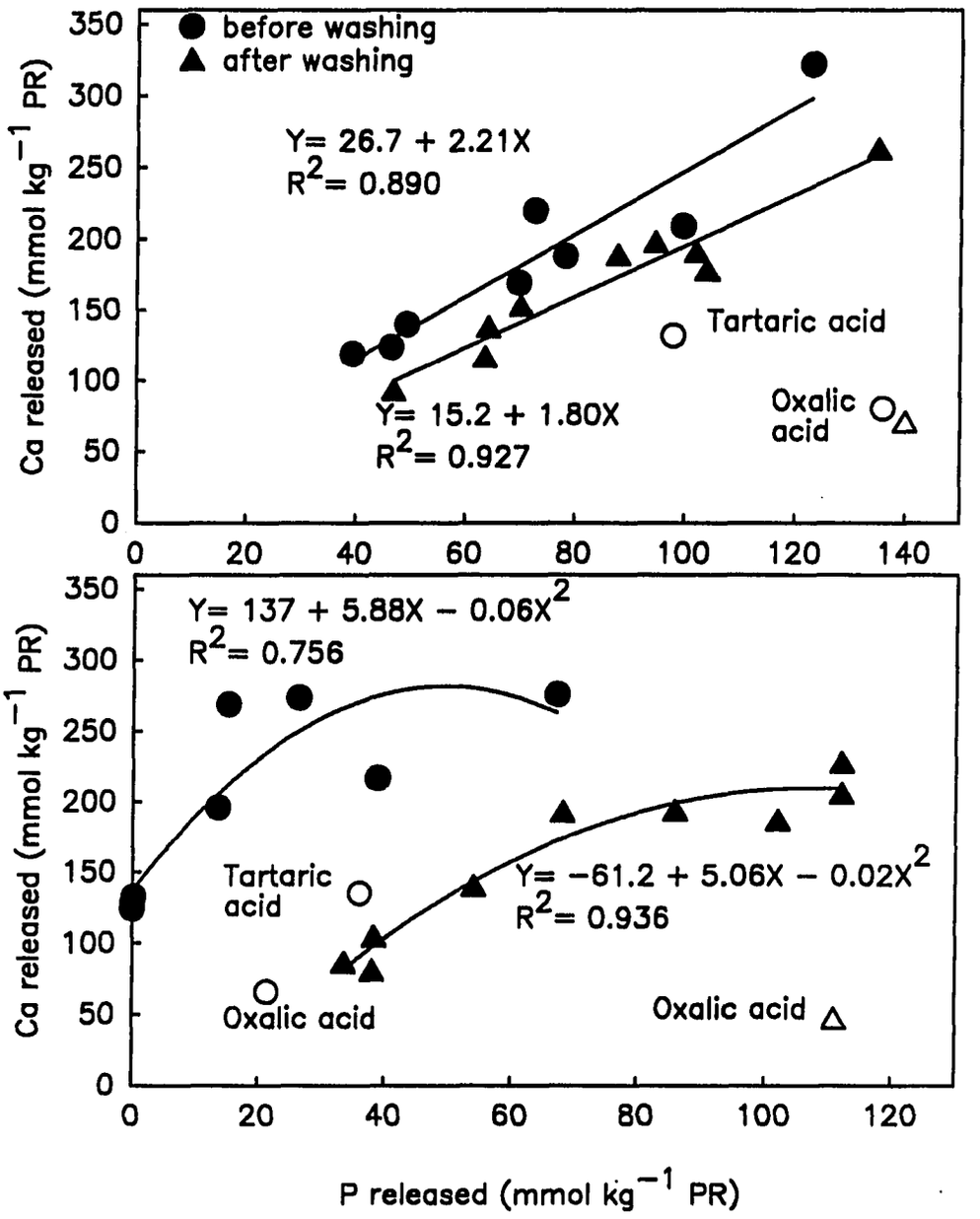


Figure 24. Relationships between Ca and P released from Central Florida (top) and Sechura (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

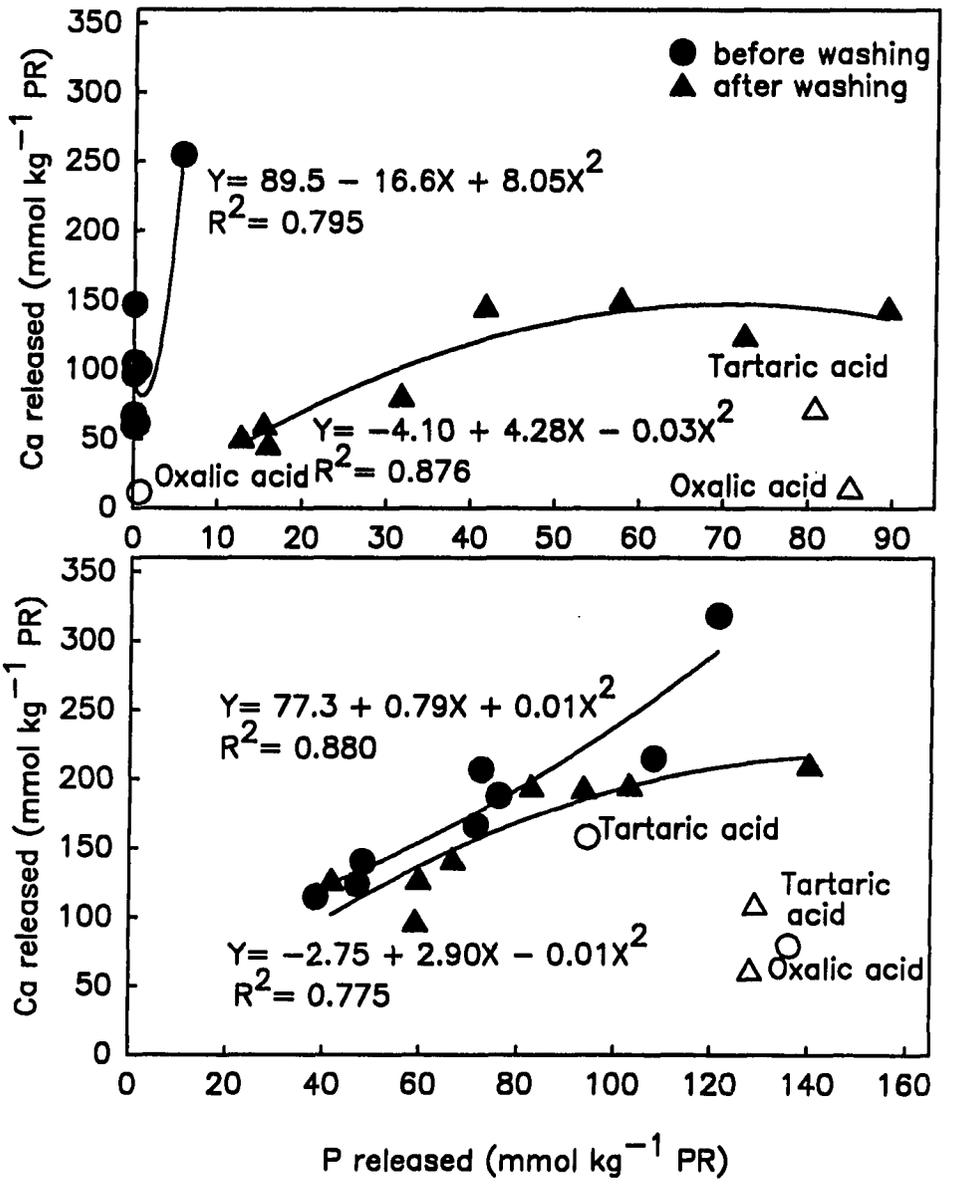


Figure 25. Relationships between Ca and P released from Minjingu (top) and North Florida (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

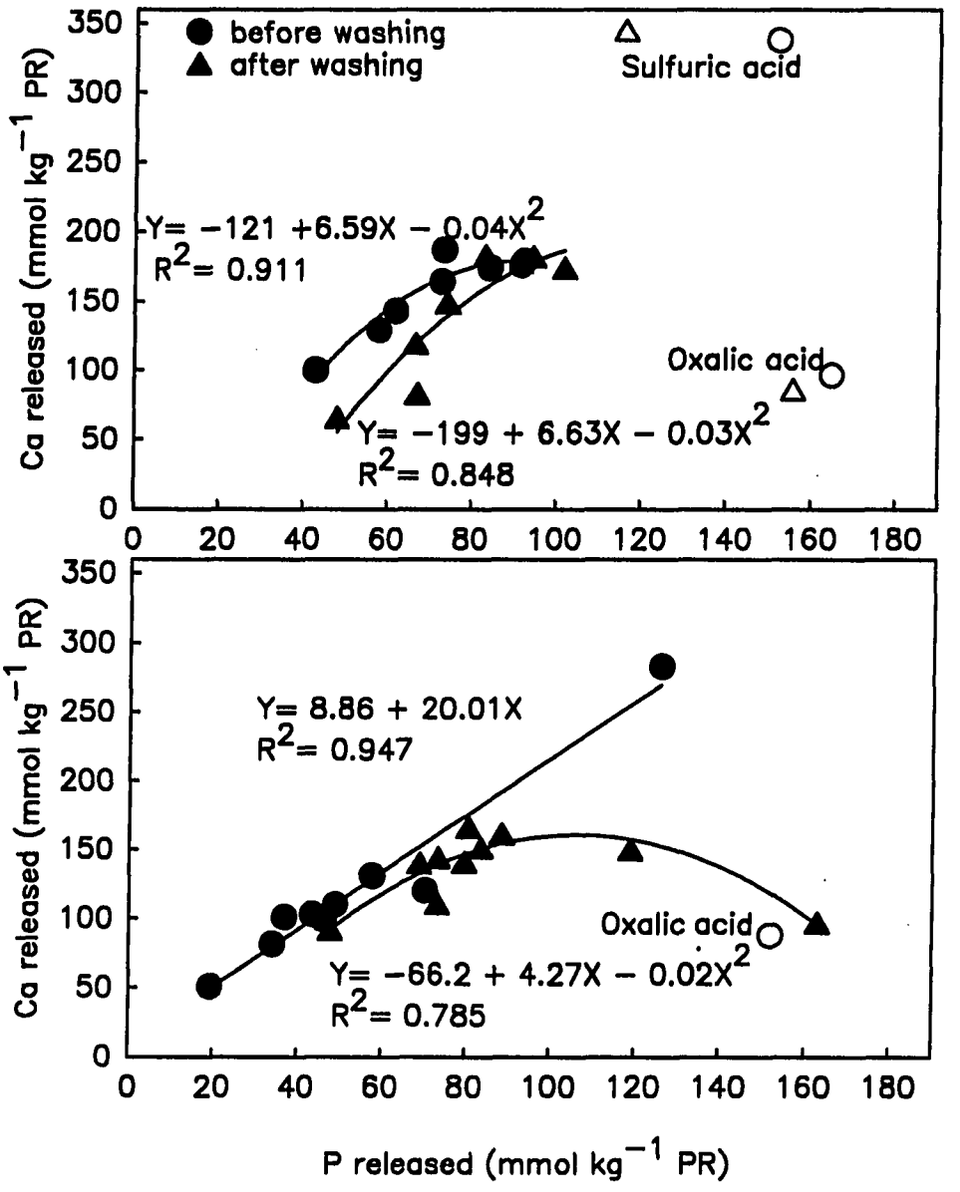


Figure 26. Relationships between Ca and P released from Hahotoe (top) and Parc W (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

correlated with P released for all the 12 PRs studied, with the exception of Minjingu PR before free carbonate removal (Figure 31). Indeed, before free carbonate removal, no P or very little P was released from this rock; a high regression coefficient (R^2 = 0.830), however, was obtained between P and Mg after free carbonate removal.

The relationships between P and Al released from the 12 PRs with the acids without free carbonate removal are plotted in Figures 33-38. The individual values are summarized in the Appendix (Tables 27 and 28). The inorganic P released was positively correlated with the amounts of Al released for all low reactive PRs (Figures 33 and 34). The stability constants compiled in Table 10 show that the organic acids studied formed more stable complexes with Al than with Ca. This suggests that the role of aluminum phosphates (even in small amounts) cannot be underestimated. No relationship was found between P and Al released for medium and high reactive PRs (Figures 35-38), with the exception of the Central Florida PR and the North Florida PR (Figure 36).

The release of P from the PRs without free carbonate removal did not show any relationship with the amounts of Fe released (Figures 39-44), except for Kodjari PR (Figure 39) and Parc W (Figure 44). Citric acid and malonic acids appeared to form the most stable complexes with Fe. Indeed, these two acids are among the acids that have relatively high stability constants with Fe. Even though salicylic acid has the highest log K_{Fe} value (Table 12), its values did not fit the relationship; a similar result was reported by Fox et al. (1990). These results suggest that only organic acids

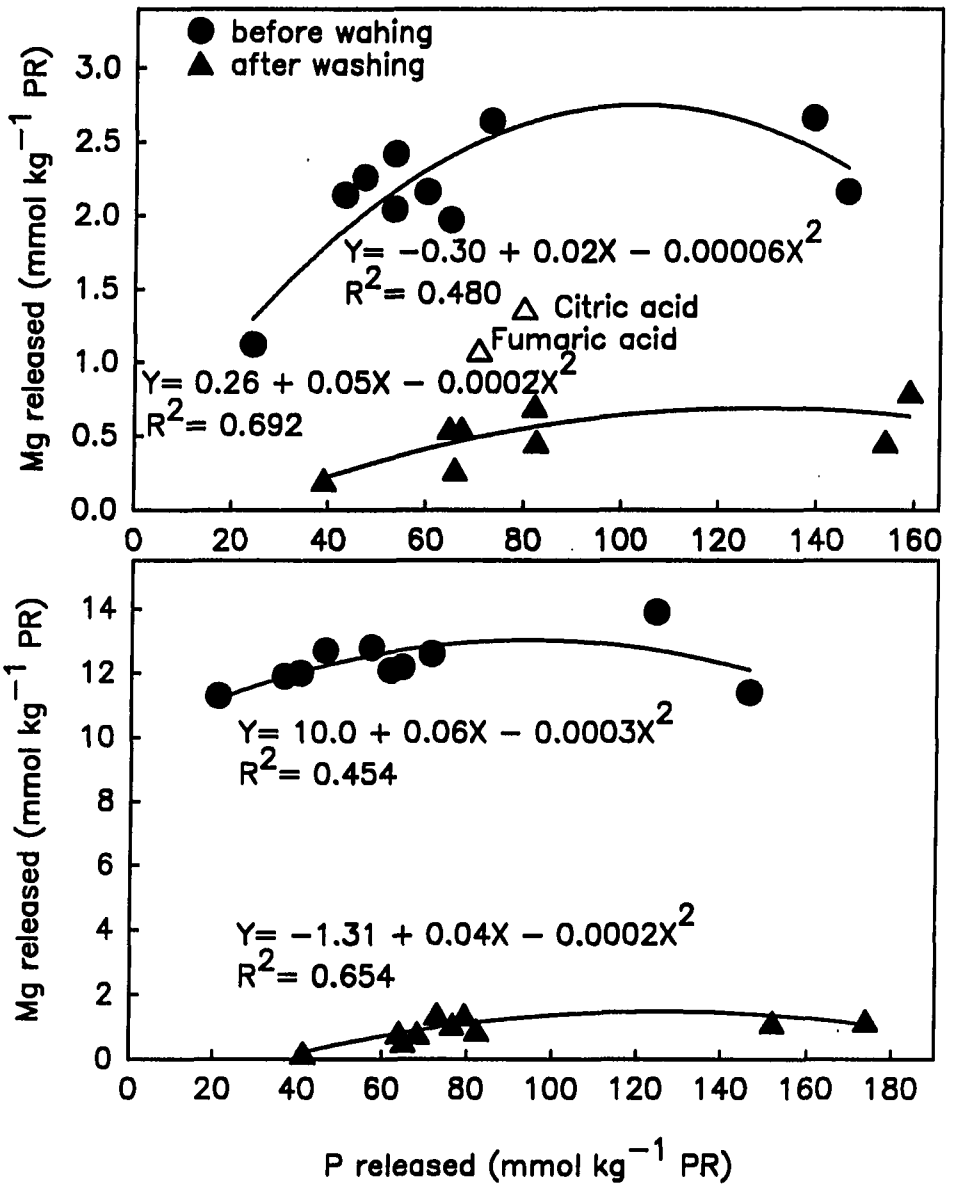


Figure 27. Relationships between Mg and P released from Kodjari (top) and Tahoua (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

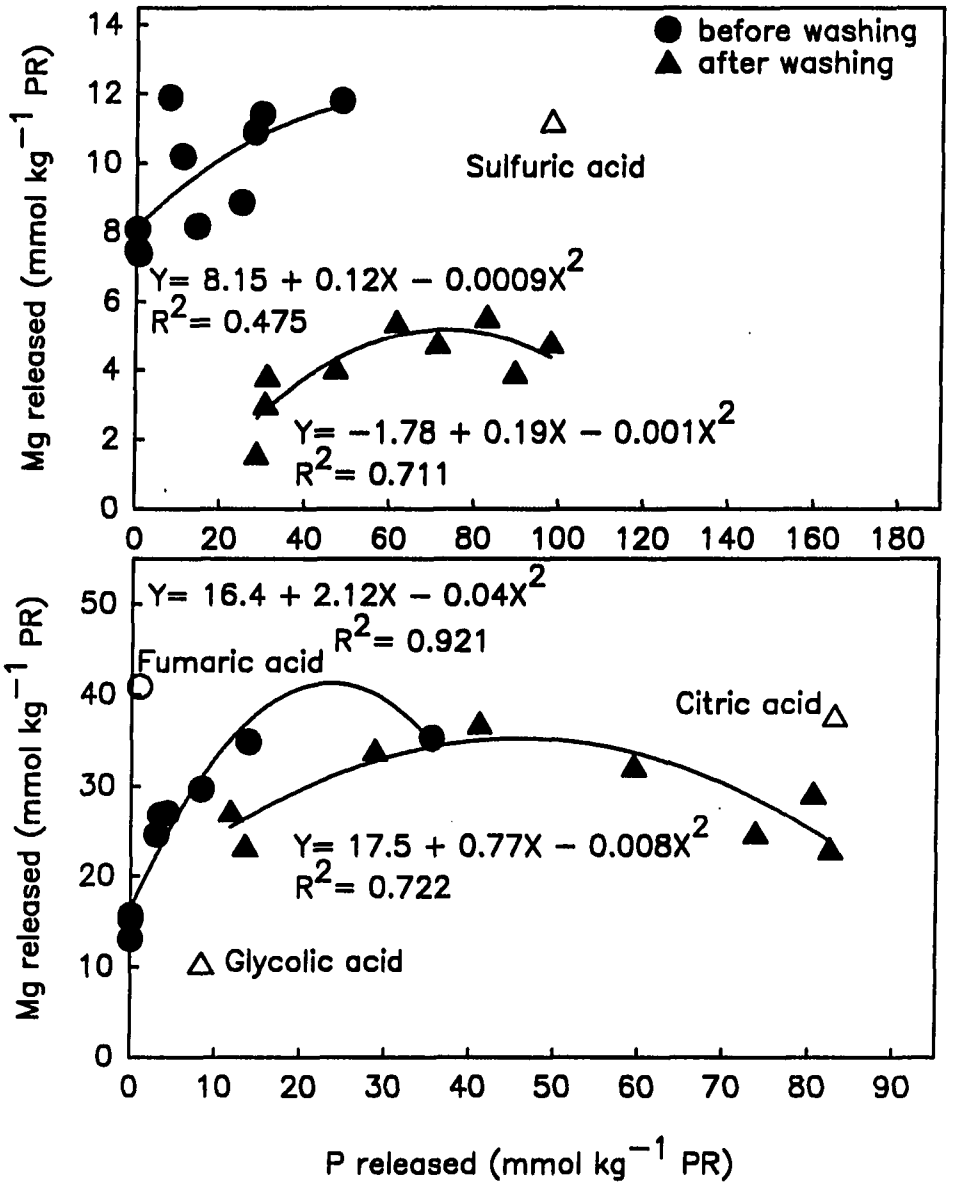


Figure 28. Relationships between Mg and P released from North Carolina (top) and Gafsa (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

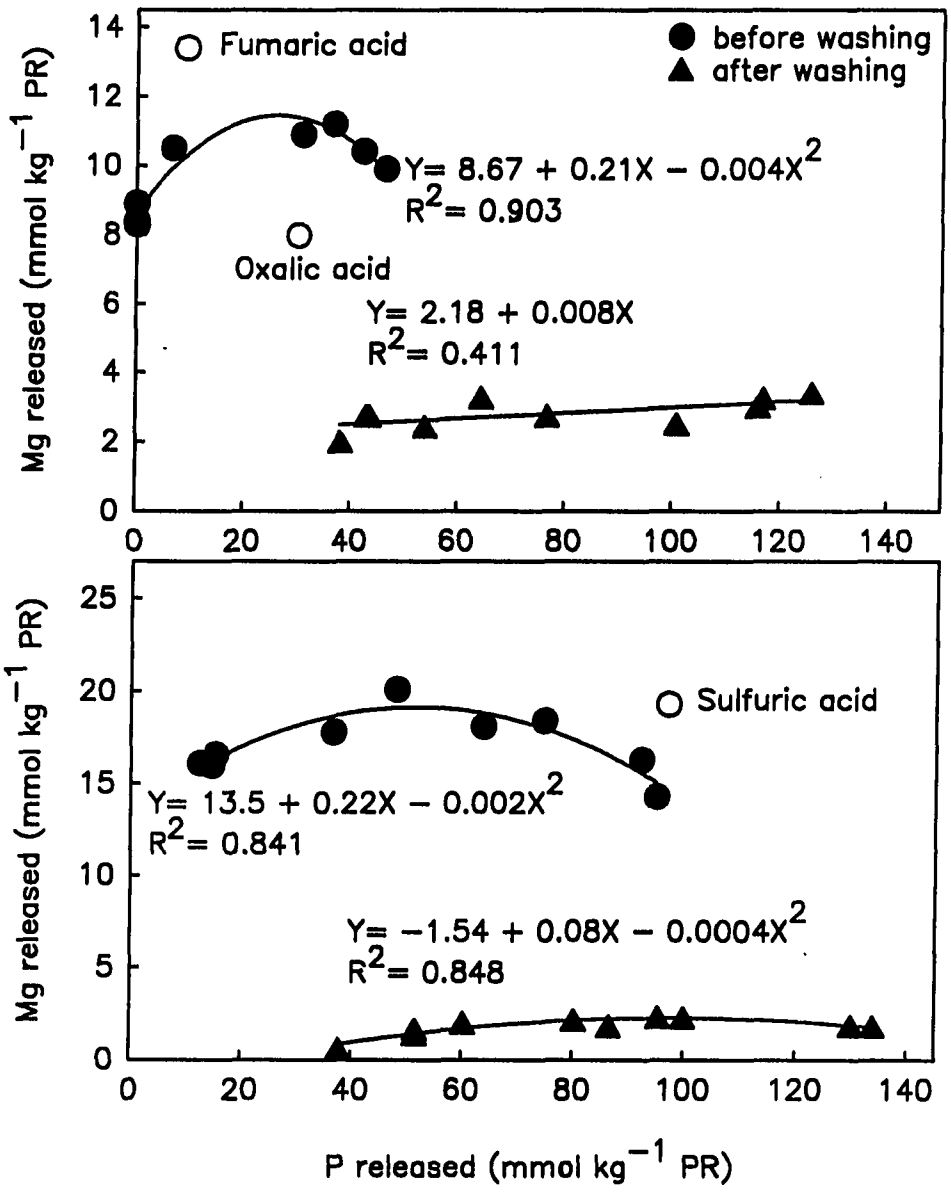


Figure 29. Relationships between Mg and P released from Khourigba (top) and Tilemsi Valley (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. Each point represents the values obtained with one acid. The open symbols were not included in the regression

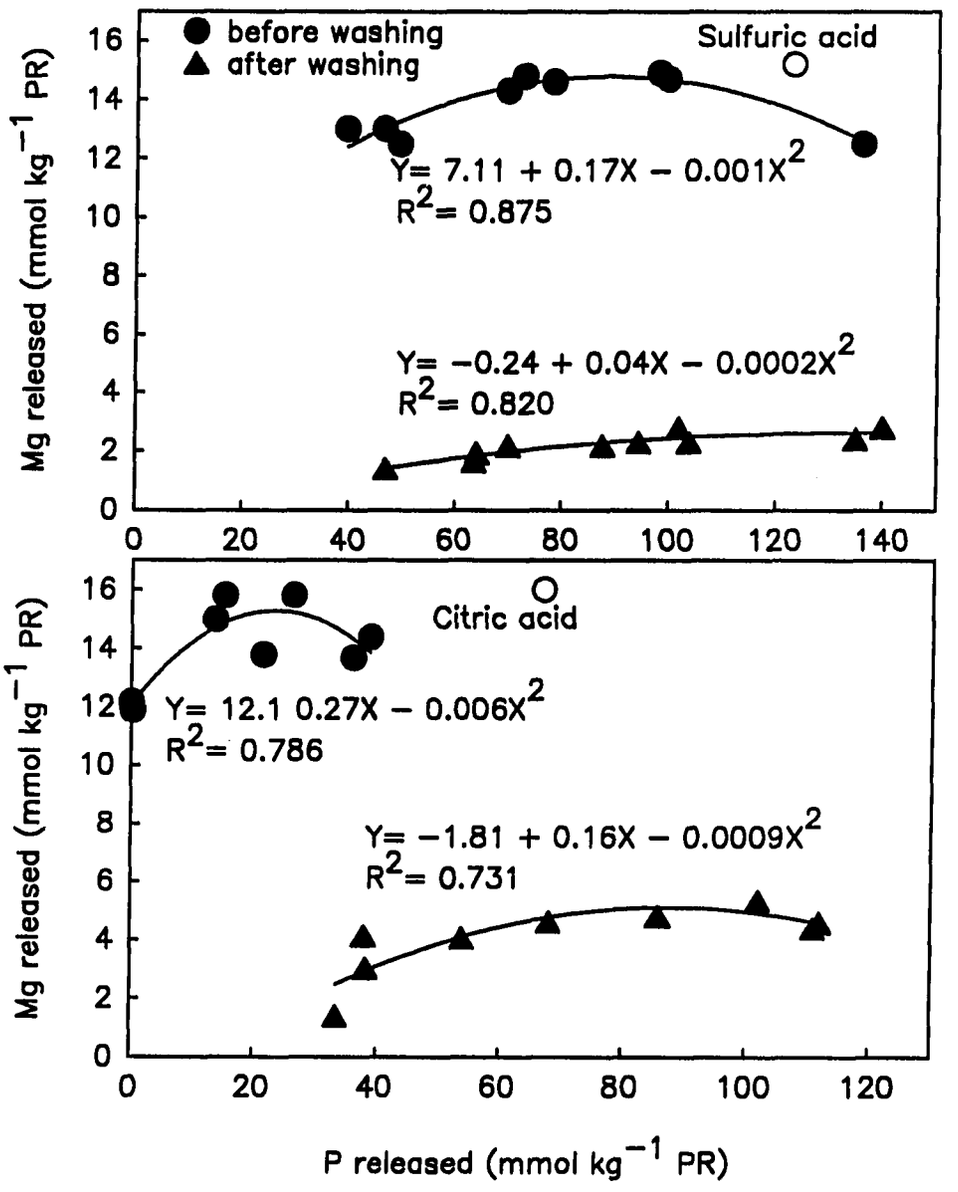


Figure 30. Relationships between Mg and P released from Central Florida (top) and Sechura (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

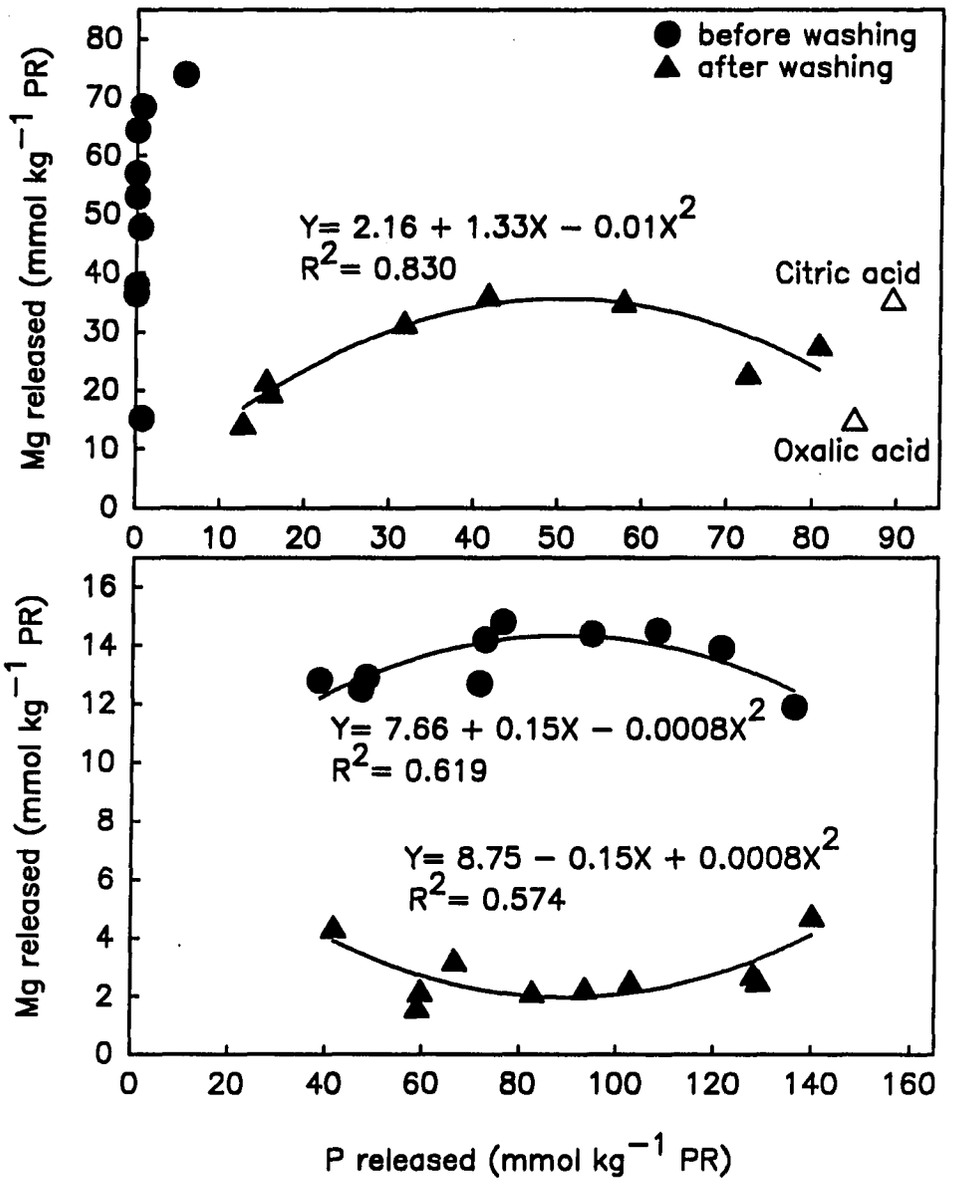


Figure 31. Relationships between Mg and P released from Minjingu (top) and North Florida (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

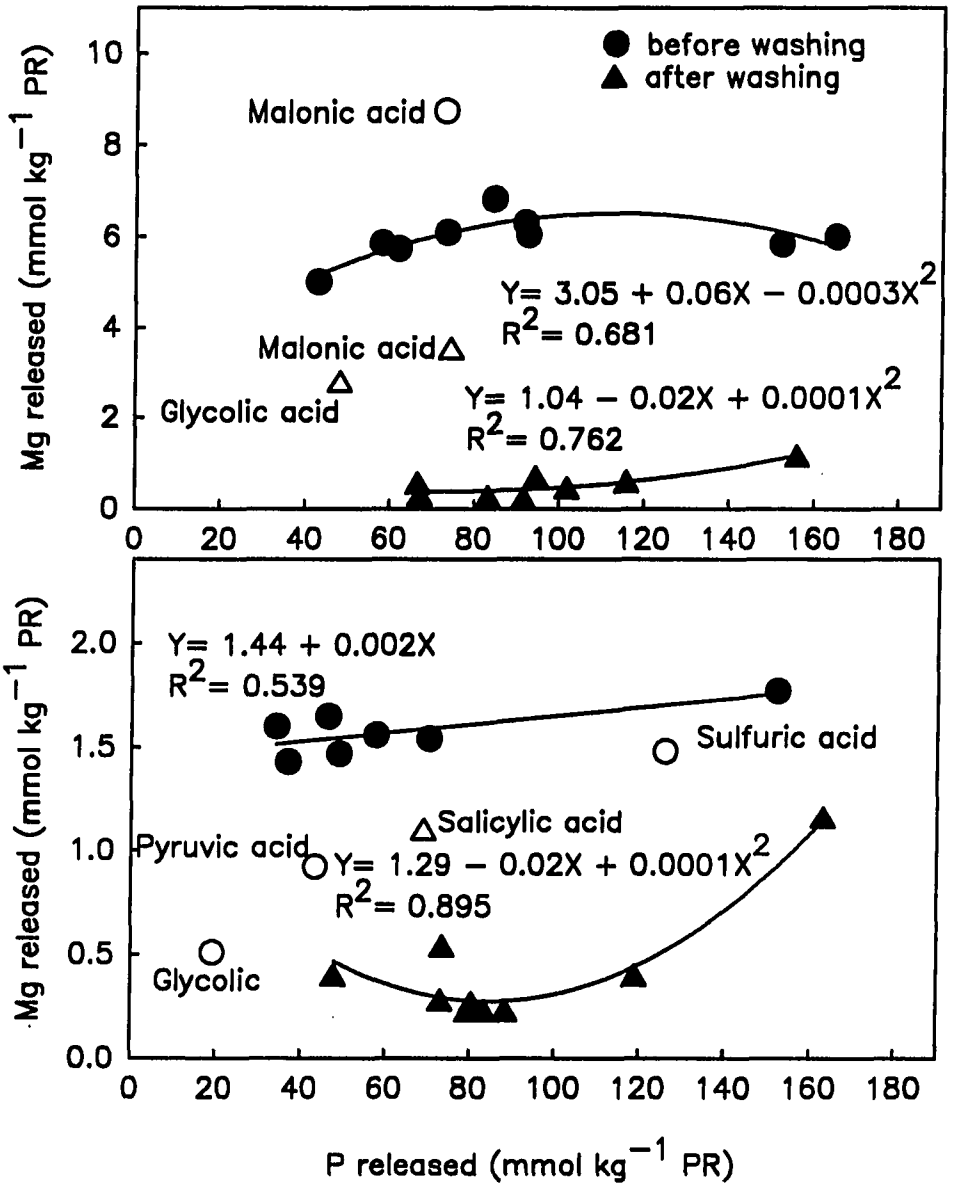


Figure 32. Relationships between Mg and P released from Hahotoe (top) and Parc W (bottom) phosphate rocks with 10 mM organic or sulfuric acid as affected by washing with 0.5 M triammonium citrate. The open symbols were not included in the regression

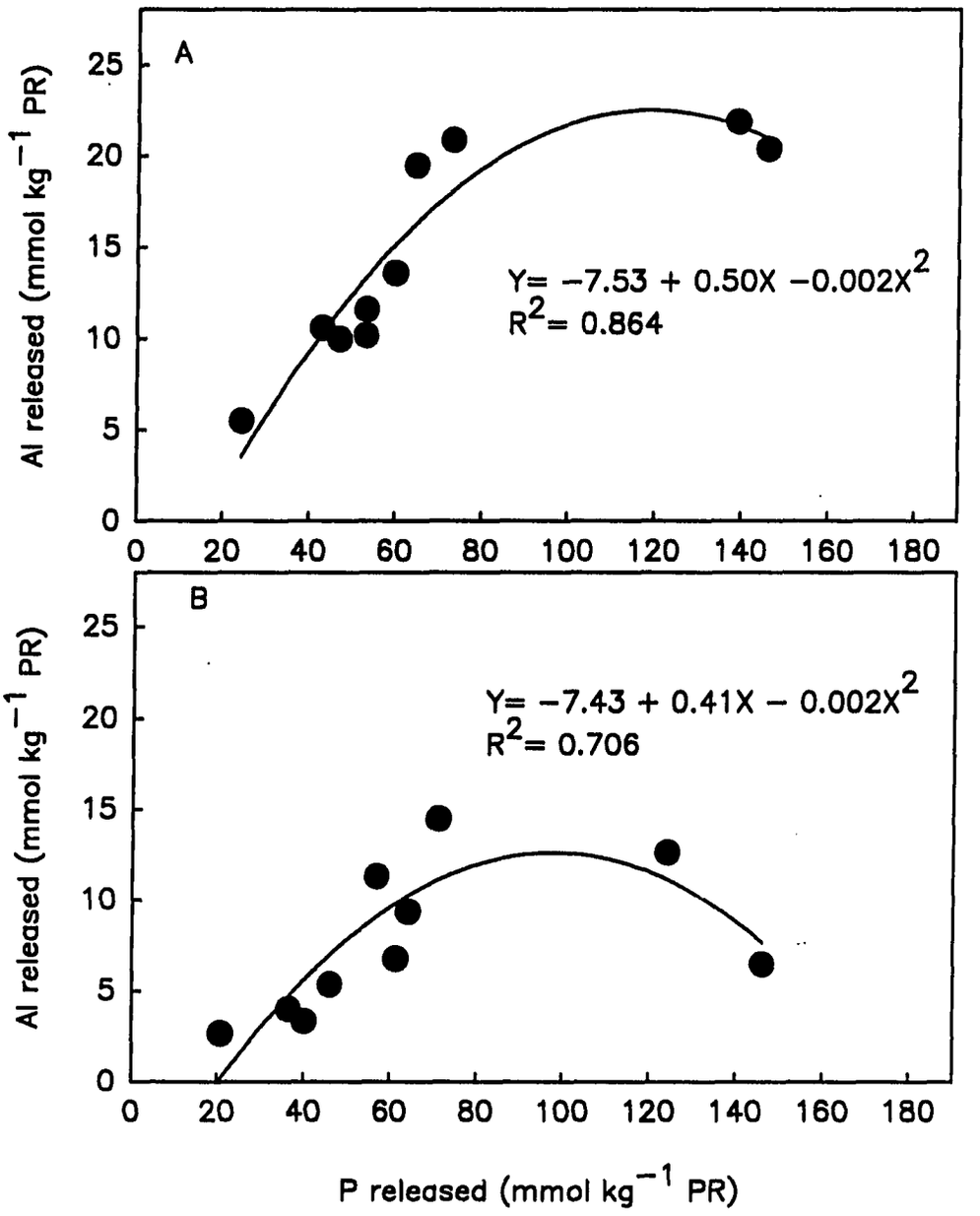


Figure 33. Relationships between Al and P released from Kodjari (A) and Tahoua (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

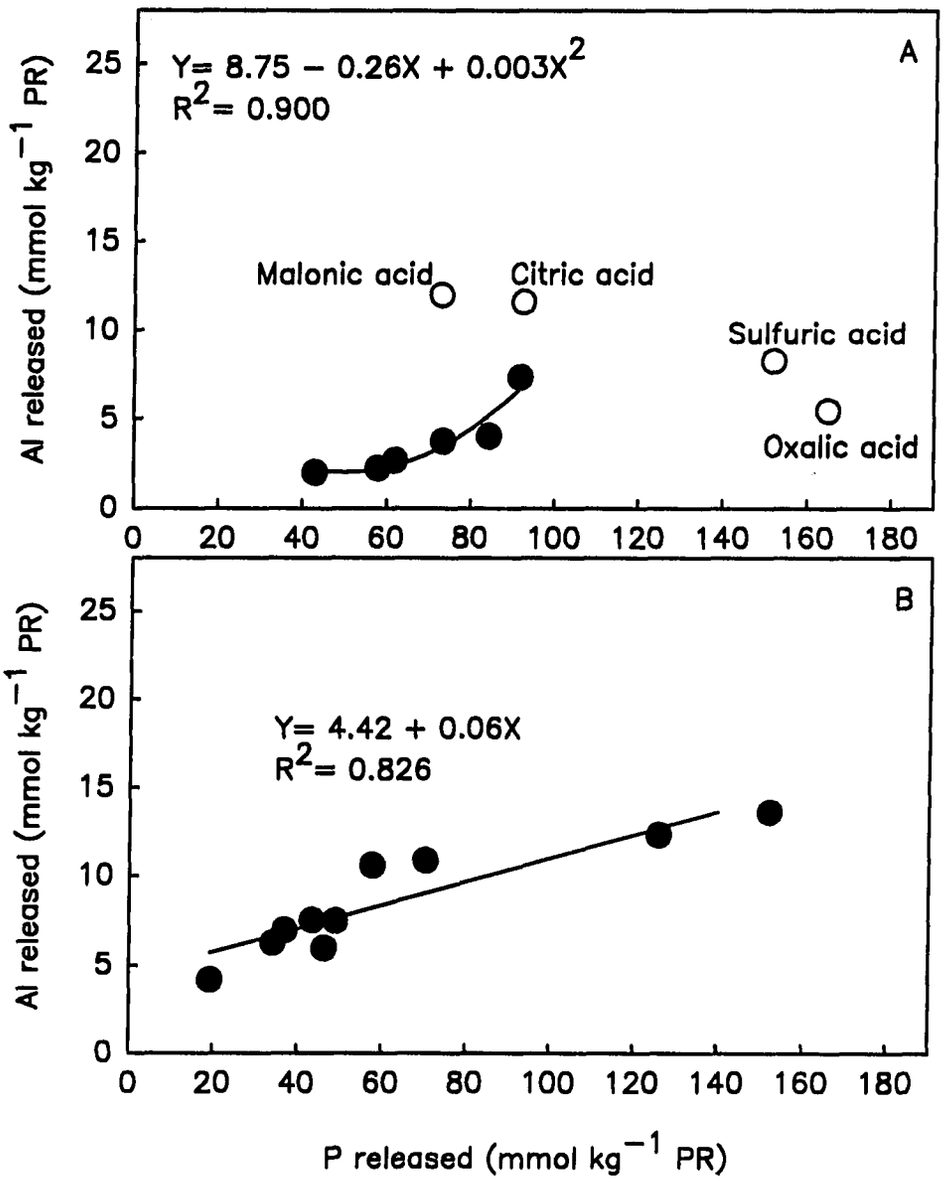


Figure 34. Relationships between Al and P released from Hahotoe (A) and Parc W (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid. The open symbols were not included n the regression

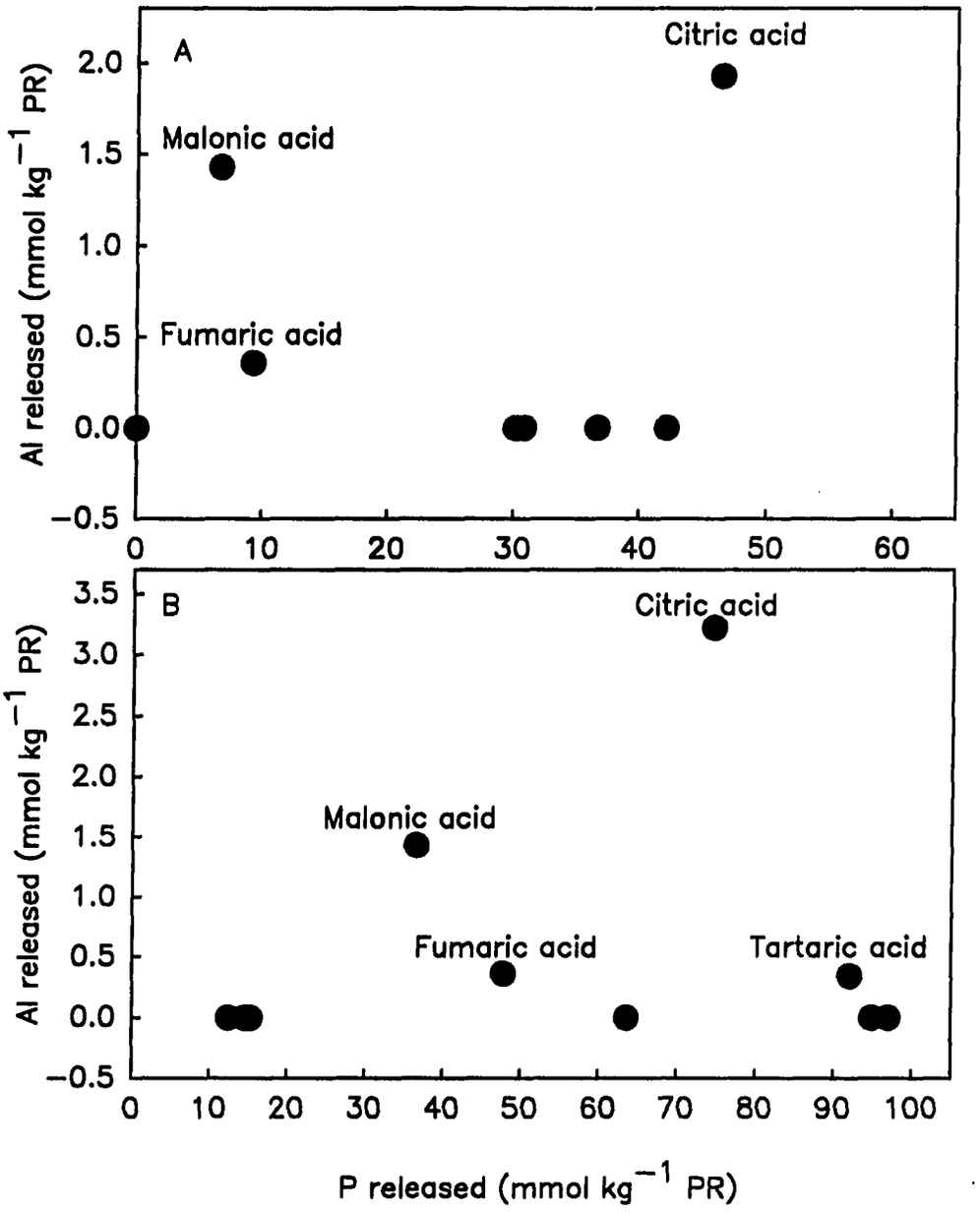


Figure 35. Relationships between Al and P released from Khourigba (A) and Tilemsi Valley (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

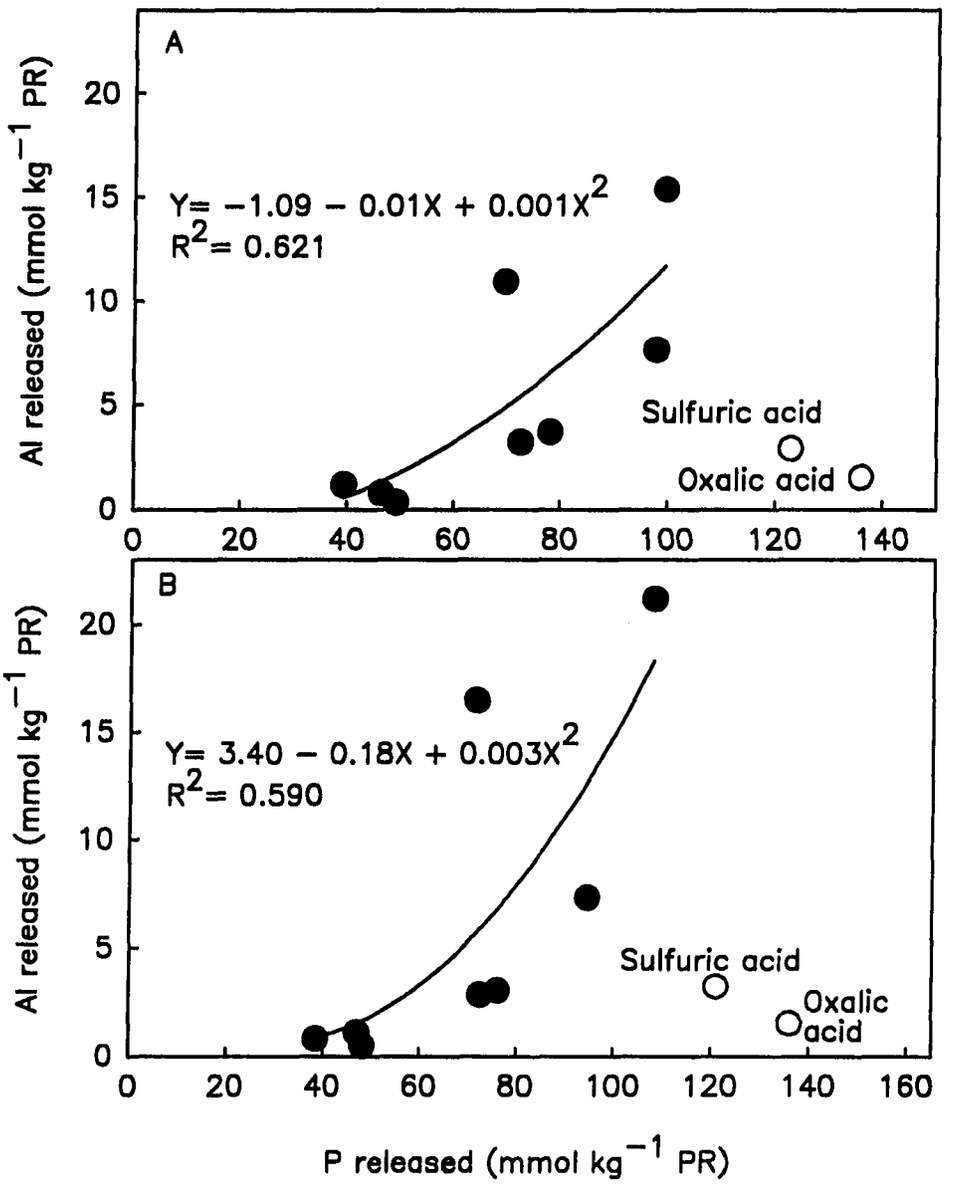


Figure 36. Relationships between Al and P released from Central Florida (A) and North Florida (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid. The open symbols were not included in the regression

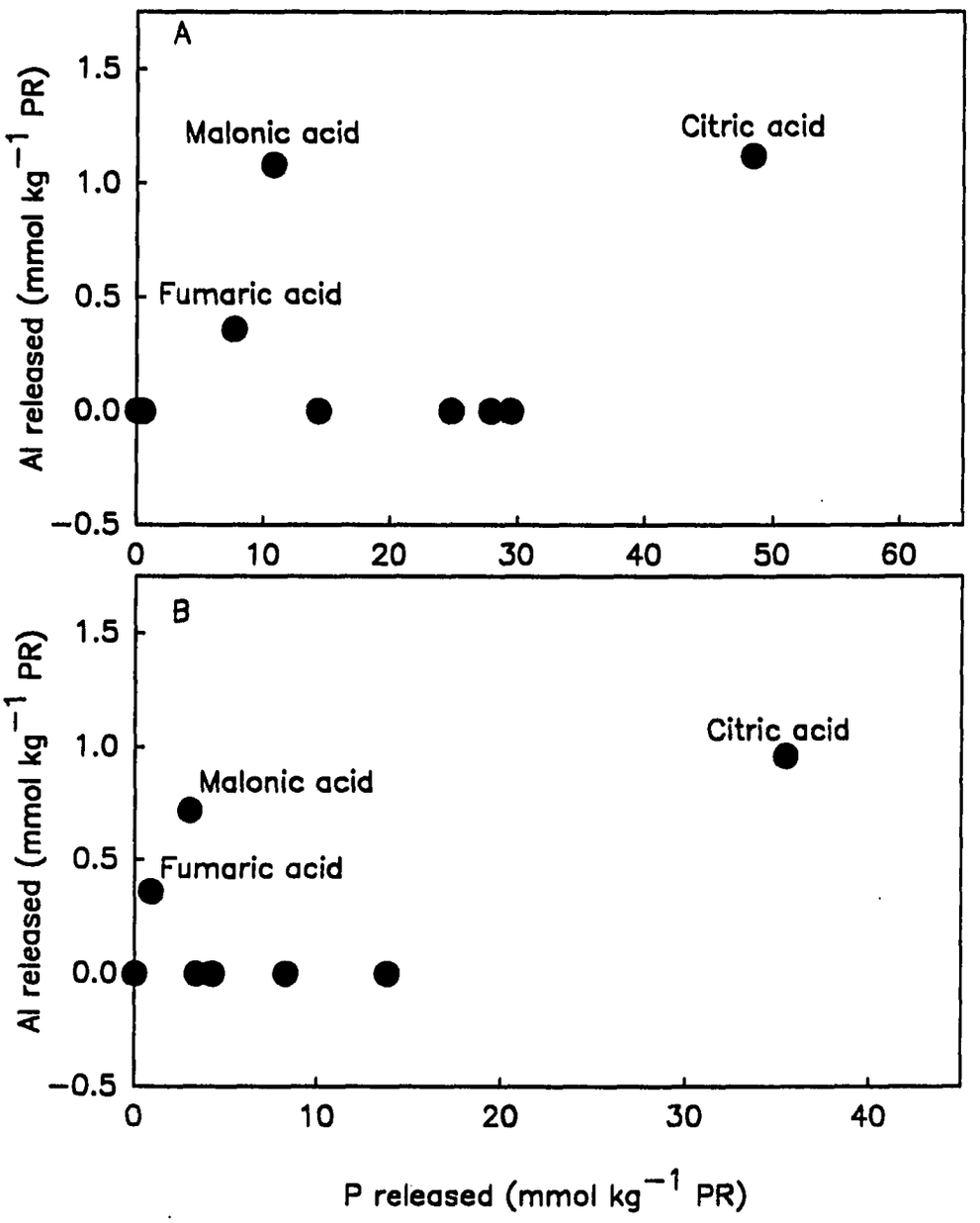


Figure 37. Relationships between Al and P released from North Carolina (A) and Gafsa (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

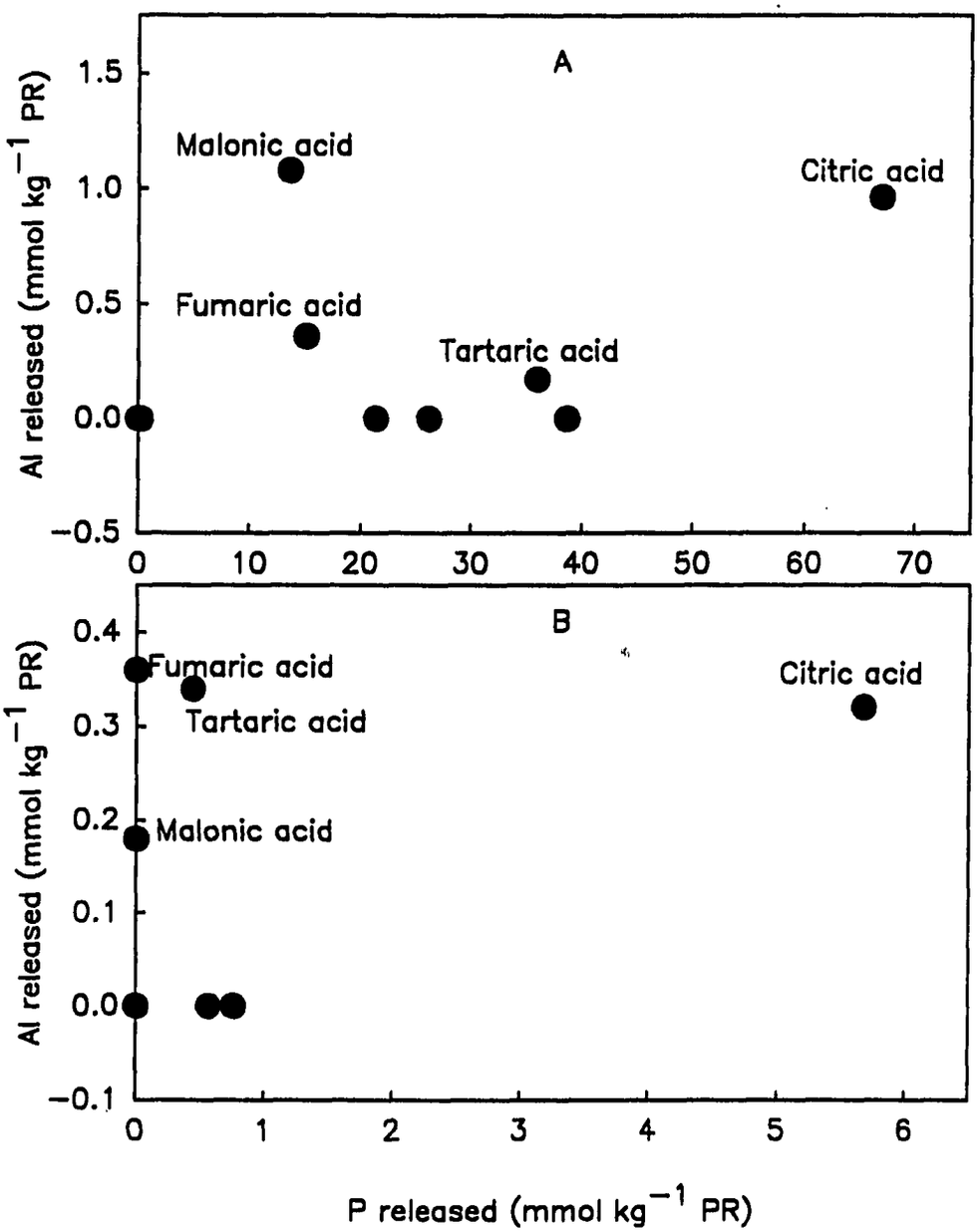


Figure 38. Relationships between Al and P released from Sechura (A) and Minjingu (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

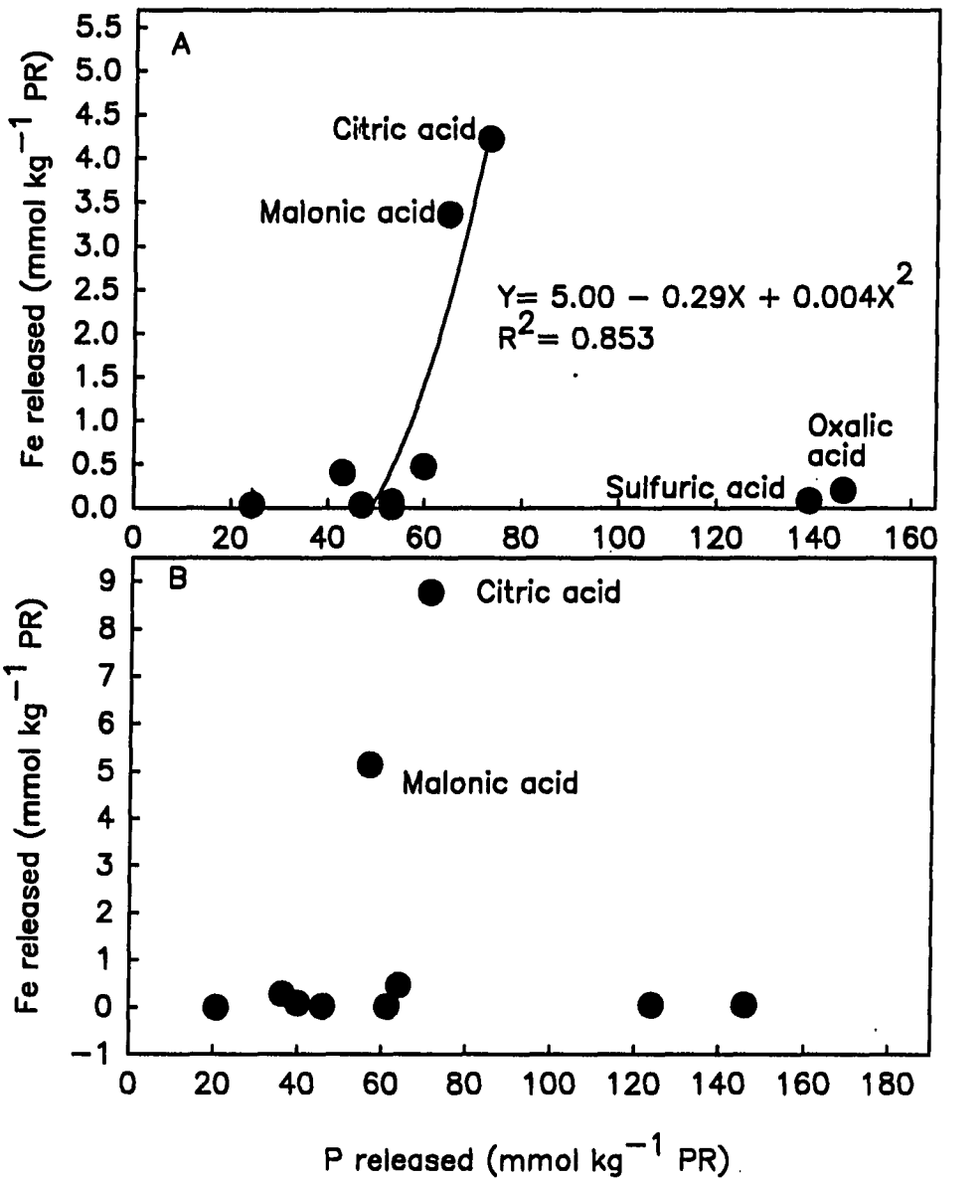


Figure 39. Relationships between Fe and P released from Kodjari (A) and Tahoua (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid. The open symbols were not included in the regression

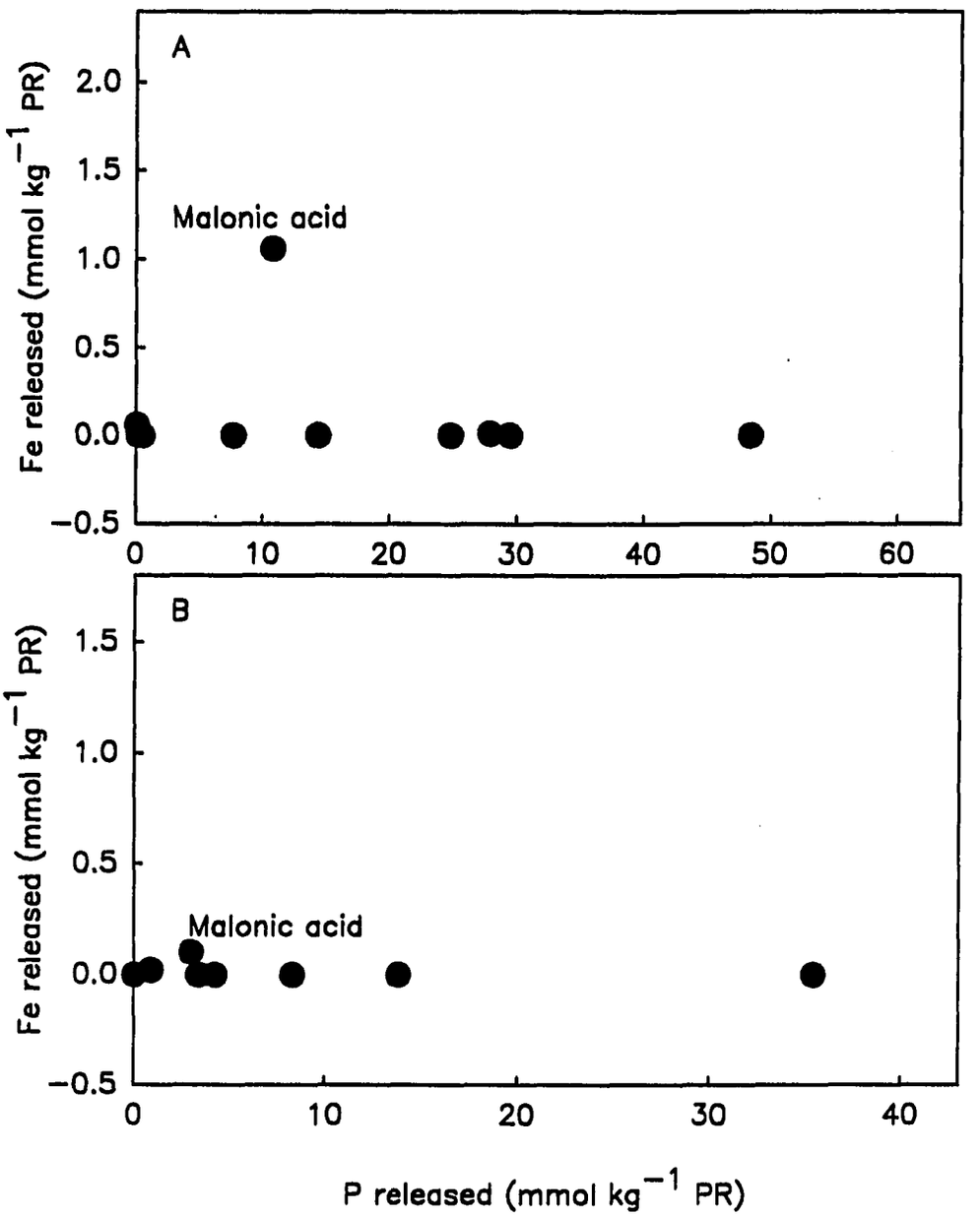


Figure 40. Relationships between Fe and P released from North Carolina (A) and Gafsa (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

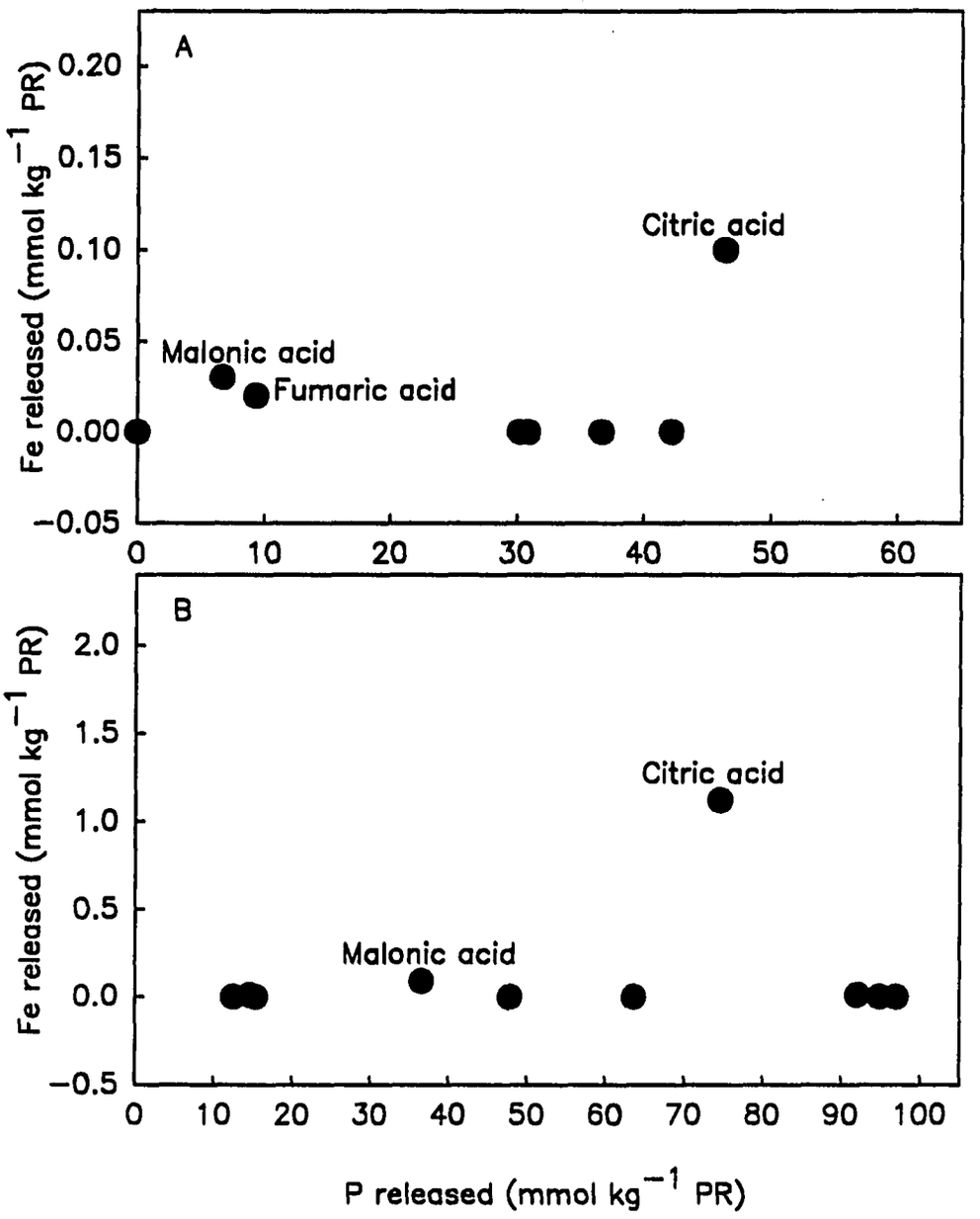


Figure 41. Relationships between Fe and P released from Khourigba (A) and Tilemsi Valley (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

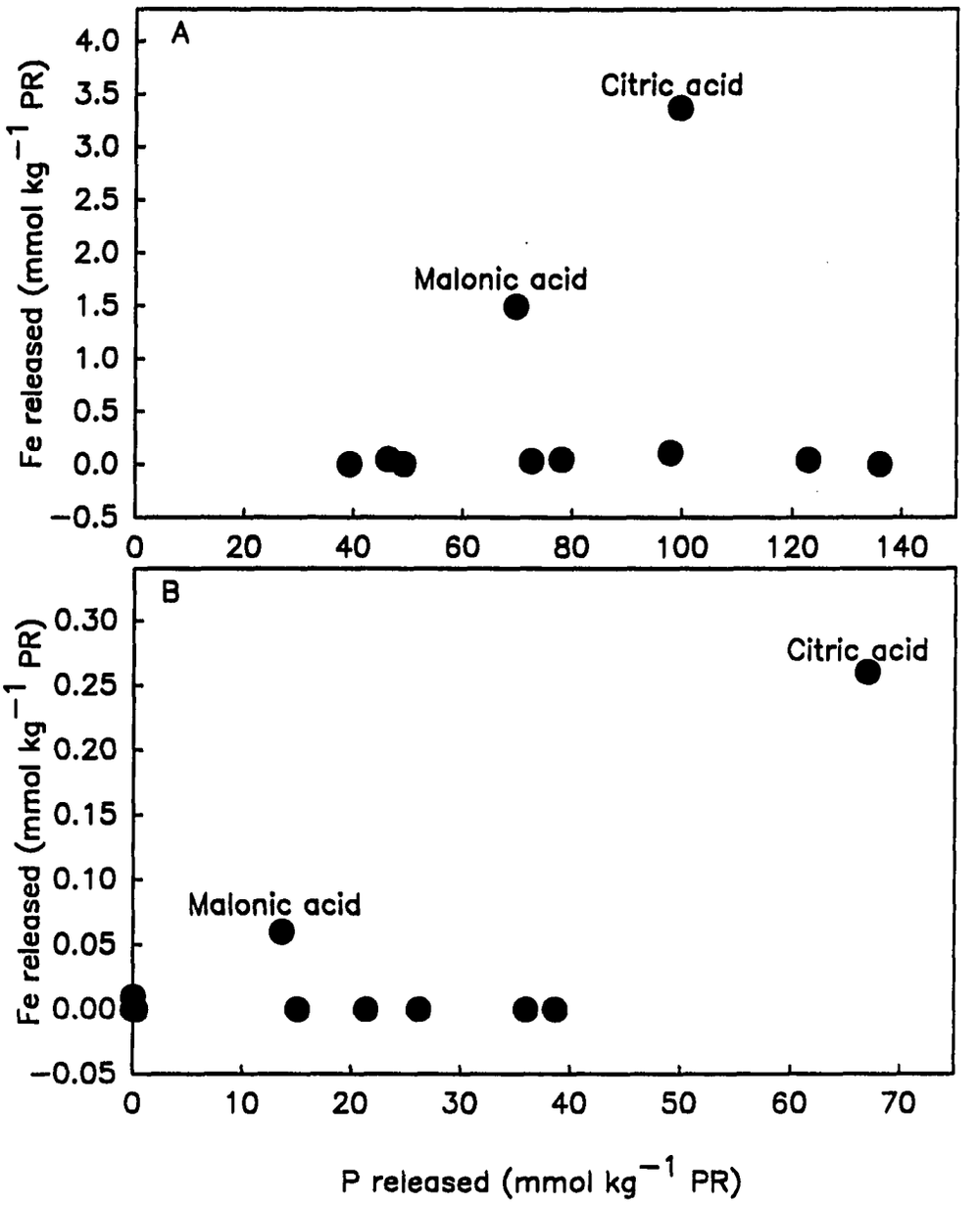


Figure 42. Relationships between Fe and P released from Central Florida (A) and Sechura (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

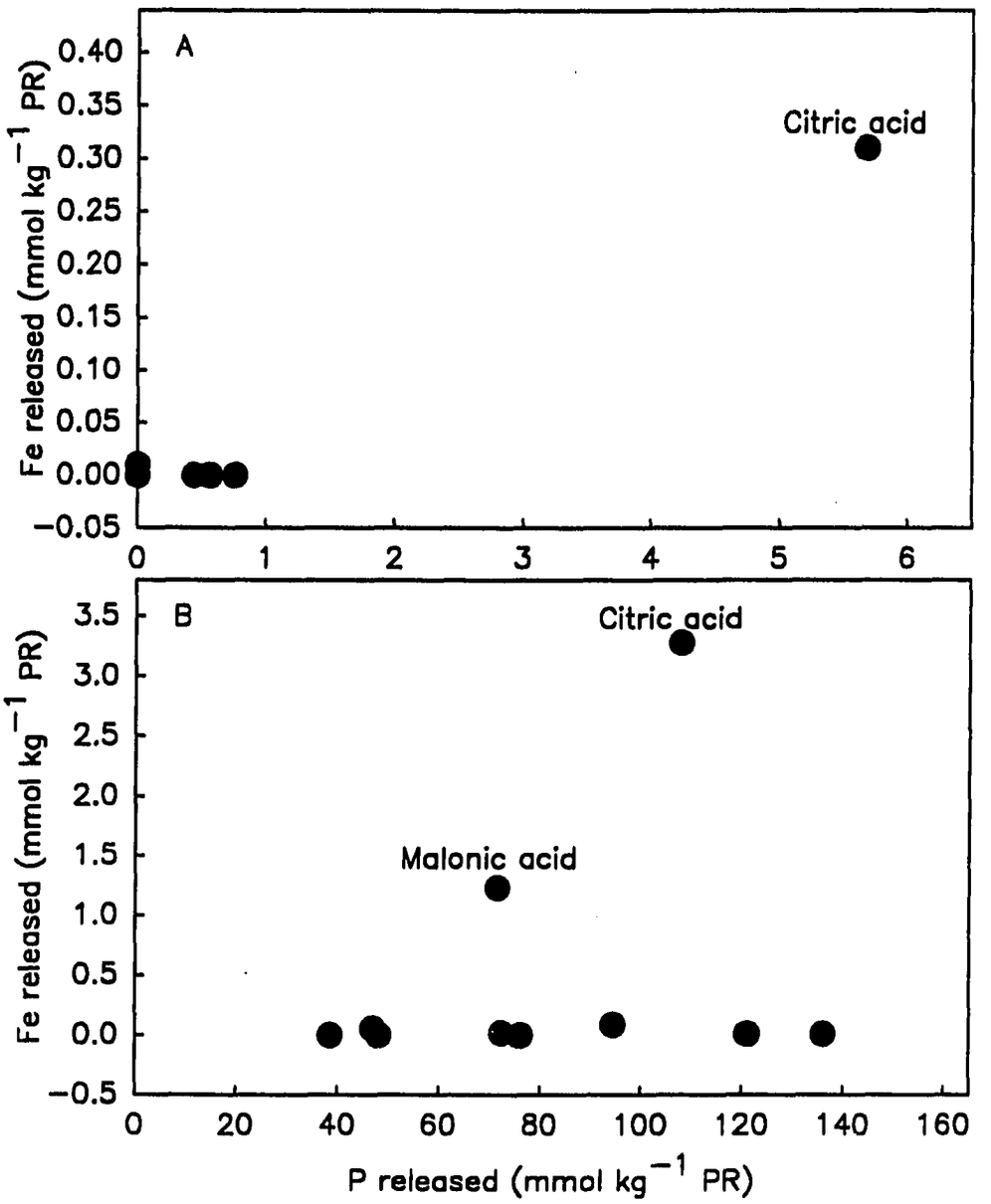


Figure 43. Relationships between Fe and P released from Minjingu (A) and North Florida (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid

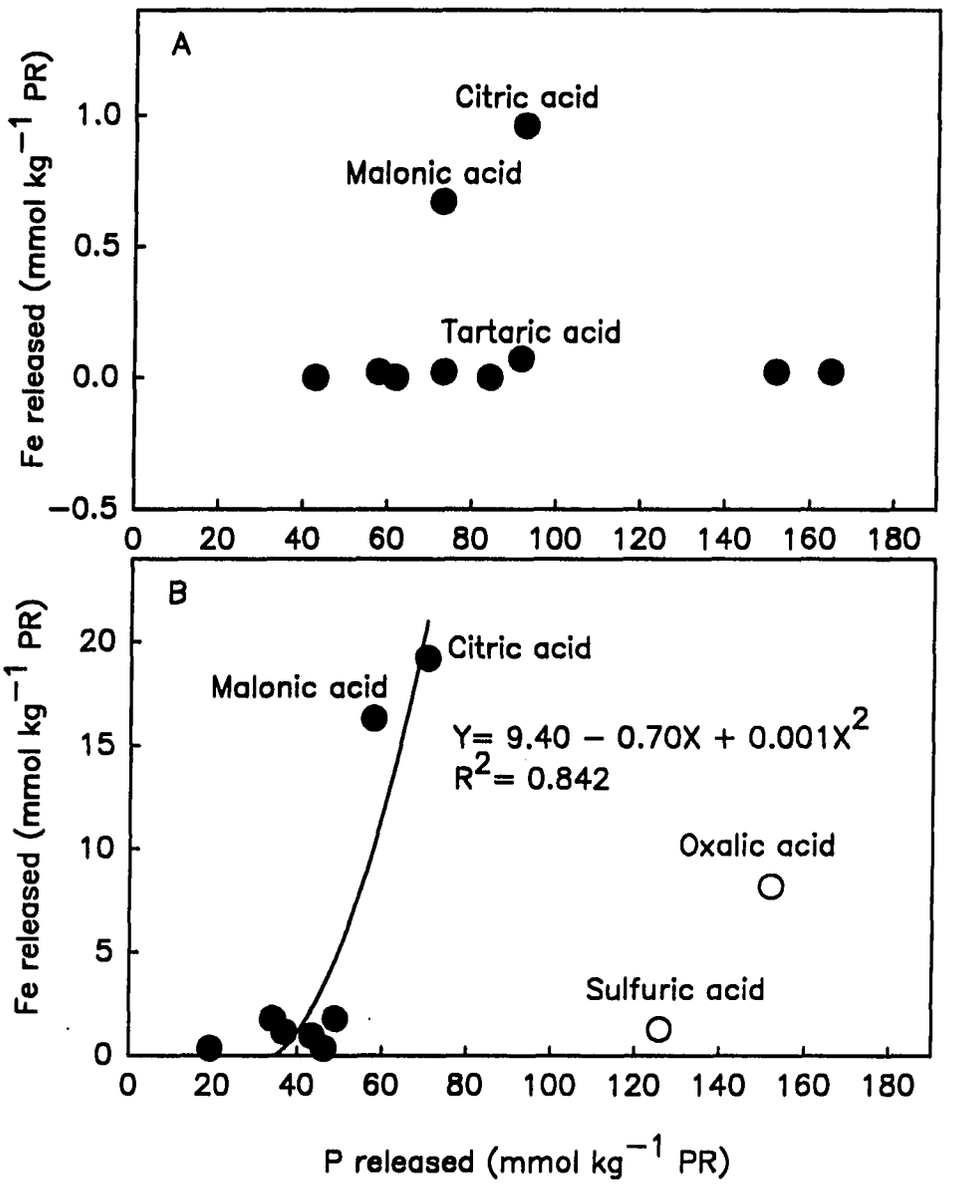


Figure 44. Relationships between Fe and P released from Hahotoe (A) and Parc W (B) phosphate rocks with 10 mM organic or sulfuric acid. Each point represents the values obtained with one acid. The open symbols were not included in the regression

Table 12. Stability constants of organo-metallic complexes

Organic acid	Stability constant[a]		
	log K_{Al}	log K_{Ca}	log K_{Fe}
Glycolic	1.11	NA	2.90
Pyruvic	NA	0.8	NA
Oxalic	6.1	1.66	7.53
Malonic	5.24[b]	1.51	7.52
Fumaric	NA	0.48	NA
Salicylic	12.9	0.15	16.3
Tartaric	5.32	1.80	5.73
Cis-aconitic	NA	NA	NA
Citric	7.98[b]	3.5	11.5

[a]Unless otherwise specified these values were obtained from Smith and Martell (1977).

[b]Fox et al., 1990.

NA, Not available.

forming stable complexes with Al and Fe were responsible for the inorganic P released from the low reactive PRs and explain why more P was released from low than from medium and high reactive PRs.

In light of the results reported here, it appears that free carbonate removal or digestion of the rock with triammonium citrate solution prior to P extraction increases the P released from PRs independently of their reactivity; the amount of the increase due to free carbonate removal was related to free carbonate content of the rocks. Jurinack et al. (1986) showed that increase in carbon dioxide in solution depresses hydroxyapatite solubility. The necessity for the free carbonate removal from PRs was also stressed by Smith and Lehr (1966). The amounts of P released from the PRs studied by the different organic acids varied considerably among the rocks. The effectiveness of the organic acids to release P from PRs seems to be related to the structure, the position of the functional groups, and to the formation of stable organo-metallic complexes. It was noted that dicarboxylic and tricarboxylic acids were the most effective. The number of carboxyl groups is, therefore, an important factor in the complexation reactions. Citric and cis-aconitic acids are both α, β, γ tricarboxylic acids; in addition to the COOH groups, citric acid has a β-hydroxyl group that made citric acid more effective than cis-aconitic. It is worth noting that oxalic acid, a dicarboxylic acid, was more effective than all the organic acids used at 10 mM concentration. When these acids were used at 1 mM concentration (Figure 5), citric acid was more effective than oxalic acid in releasing P. Similar results were obtained

by Harrold (1992) on Nicollet and Lester soils. The reason for the greater release of P by oxalic acid than by citric acid is that the former forms a stable Ca phase (calcium oxalate precipitate), which is more effective than a Ca complex formed by the latter (Jurinak et al., 1986). Only oxalic acid was consistently more effective (sometimes citric and tartaric acids) or equally as effective as sulfuric acid in releasing P; this suggests that the acidic effect of mineral acids in P release from PRs should not be underestimated. Finally, the greater release of Al and Fe from low reactive PRs by the organic acids explains the greater release of inorganic P from these rocks.

PART III. EFFECT OF ORGANIC ACIDS ON THE RELEASE OF PHOSPHORUS FROM PHOSPHATE ROCKS ADDED TO SOILS

INTRODUCTION

The main obstacle for direct application of PR to soils is the failure of PRs to release P into the soil solution in quantity enough to support plant growth. Even though some PRs (e.g., North Carolina, Central Florida, Sechura, Gafsa, and Khouribga) have been known to be very effective in releasing P into soil solution, the vast majority of PRs are ineffective in releasing P when applied to soils. Two organic acids (citric and formic) have been widely used in laboratory studies to predict solubility of phosphate rocks. While these acids in various forms and concentrations can predict the agronomic potential of PRs, they have been rarely used on soils to study the dissolution of phosphate rock in a soil medium. There exists in the literature, to my knowledge, only one study by Chaudhary and Mishra (1980) on transformation of PR in soil in the presence of citric and oxalic acids. Considerable evidence (Cromack et al., 1979; Johnston, 1959; and Moghimi et al., 1978) indicated that organic acids can effectively chelate Ca, Al, and Fe of phosphate-bearing minerals and increase release of P (Part II). The possibility, however, exists that the P released from PR equilibrated with organic acid solution may not reflect the P released when PR-organic acid mixture is applied to soil. Therefore, the objective of this study was to investigate the effect of mixing organic acid powder with PR on the release of plant-available P in soils.

MATERIALS AND METHODS

Soils

Surface (0-15 cm) samples of Gosport soil (fine, illitic, mesic Typic Dystrochrepts), Clinton soil (fine, montmorillonitic, mesic Typic Hapludalfs), and Grundy soil (fine, montmorillonitic, mesic Aquic Arginolls) were collected in the State of Iowa. The Gosport soil was obtained from a pasture in Mahaska country; Clinton soil was obtained from a land under conservation in Mahaska county; and Grundy soil was obtained from a farm under conservation in Marion county. These soils were passed through an electric-powered shredder (Linding Manufacturing Corporation) fitted with a 1.5 cm screen. The moist sieved soil was placed in polyethylene bags and stored at room temperature (ca · 23°C) in the agronomy greenhouse. Each soil was air dried and ground to pass a 2-mm mesh, while another portion was ground to pass a 80-mesh (180 μm) screen. These soils were selected for their low available P content. Selected chemical and physical properties of these soils are reported in Table 13. In the analyses reported in Table 13, pH was determined by a combination glass electrode (soil:water or 0.01 M $CaCl_2$ ratio, 1:2.5). Total N was determined by using the Kjeldahl method described by Keeney and Nelson (1982). Total P was determined by the perchloric acid digestion method of Olsen and Dean (1965). Available P was determined by the Bray I method of Bray and Kurtz (1945) and by the iron-hydroxide-impregnated filter paper (Pi) method of Menon et al. (1989a,b). Particle-size distribution was determined by using the pipette method of Kilmer and Alexander (1949). The

Table 13. Properties of soils used

Soil Series[a]	pH[b]		Organic C[c]	Total N	Phosphorus			Clay	Sand
	H_2O	$CaCl_2$			Total	BrayI	P_i		
			g kg^{-1}	---------- mg kg^{-1} ----------				g kg^{-1}	
Gosport	5.5	4.9	23.7	2040	610	1.6	7.0	256	296
Clinton	6.0	5.7	16.5	1630	476	6.2	6.5	312	19
Grundy	5.8	5.4	13.4	1181	445	3.6	5.9	293	13

[a]Subgroups: Gosport, Typic Dystrochrepts; Clinton, Typic Hapludalfs; Grundy, Acquic Argiudolls.

[b]Soil:water or soil:0.01 M $CaCl_2$ ratio, 1:2.5.

analyses for total N and total P were carried out on < 80 mesh, whereas all other analyses were performed on < 2 mm samples.

Procedures

The laboratory incubation study to investigate the effect of organic acids on the release of P from PRs added to soils was carried out as follows. A phosphate rock sample and an organic acid ground separately into powder form (< 100 mesh) were mixed in appropriate amounts with glass beads (Cataphote Division, Ferro Corp.,

Jackson, Mississippi) of similar size to give 200 mg P kg^{-1} soil and 50 mmol acid kg^{-1} PR. Preliminary studies with different rates of organic soil and PR showed that 50 mmol organic acid kg^{-1} PR released more P than the other rates tested (10, 20, 30, and 40 mmol kg^{-1} PR). The fertilizer material thus prepared was placed as a layer in 2 g of air-dried soil (< 2 mm) weighted out into a pyrex culture tube (16 x 150 mm). A few drops of deionized water was added to the tube to give a moisture content of about 50-60% of the water-holding capacity of the soil. The tube was then covered with parafilm film perforated in the center for aeration. Duplicated tubes were incubated at 25°C±1°C for 0, 15, 30, or 45 days. The moisture in the tube was monitored weekly and additional water was added when necessary to keep the soil moisture constant in the tube. Controls with PR without organic acid or with organic acid without PR were included. At the end of the incubation, plant-available P, estimated by the P_i filter paper method described by Menon et al. (1989a, b), was used to compare the P release from PR and PR-organic acid mixture. For this purpose six PRs (Kodjari, North Carolina, Gafsa, Tilemsi Valley, Central Florida, and Hahotoe) and four organic acids (oxalic, tartaric, cis-aconitic, and citric) were used. The percentage of P released from PR added to soil was calculated by using the following equation:

$$\text{Percentage of P released} = \frac{(A - B)}{C} \times 100,$$

where A is the amount of inorganic P released from the PR mixed with or without organic acid added to soils; B is the amount of inorganic P released from the control treatments (no PR added but with or without organic acid), and C is the amount of P applied.

RESULTS AND DISCUSSION

Estimation of Plant-Available Phosphorus in Soils

Laboratory experiments (Parts I and II) showed that low-molecular-weight organic acids may release considerable amounts of P from PRs; but the amount of available P released for plant uptake by the organic acids from PRs is not known. Plant-available P was estimated by the P_i filter paper method of Menon et al. (1989a,b) by using six PR samples mixed with oxalic, tartaric, cis-aconitic, or citric acid and added to three Iowa soils. The mixture was incubated for 0, 15, 30 or 45 days. Several methods may be used to estimate plant-available P from soils; the most common include the Olsen method (Olsen et al., 1954), which is used on calcareous soils and the Bray method (Bray and Kurtz, 1945), which is used on acid soils. The Olsen method was found to underestimate plant-available P, whereas the Bray I was found to overestimate the plant-available P from soils which received PRs (Menon et al., 1989c). The P_i filter paper method (P_i test) is a relatively new method that may allow estimation of plant-available P from soils with a wide range of soil properties and was found to be the most suitable method for estimating plant-available P in soils that received PRs (Menon et al., 1989c). The method was originally proposed by Van der Zee et al. (1987) to investigate the desorption kinetics of reversibly absorbed P in Dutch soils. The P_i-test removes primary physically bound extractable P from soils and minimizes extraction of amorphous Al and Fe or Ca compounds (Sharpley, 1991). The amount of P extracted by the P_i filter paper method (P_i-P) from monocalcium

phosphate (MCP)-treated soils (Table 14) decreased with increasing incubation time. When MCP is added to soil, it dissolves and hydrolyzes to dicalcium phosphate dihydrate (DCPD) and phosphoric acid (H_3PO_4). The release of H_3PO_4 lowers the pH to 1.48, which is favorable for Fe and Al dissolution; the dissolved Fe and Al react with water-soluble P to form Al-Fe phosphate that are water-insoluble (Lindsay and Stephenson, 1959a,b). The result of these dissolution and precipitation reactions is a decrease in plant-available P from the fertilizer material (MCP). Indeed, the plant-available P decreased from 619 to 398 mg P kg^{-1} in Gosport soil, from 558 to 426 mg P kg^{-1} in Clinton soil, and from 508 to 467 mg P kg^{-1} in Grundy soil after 45 days of incubation (Table 14). The amount of P fixed varied from soil to soil; it was estimated at 221, 132, and 41 mg P kg^{-1} of Gosport, Clinton, and Grundy soils, respectively. Although the amount of extracted P from Gosport soil was the greatest (619 mg P kg^{-1} soil) at time zero, at the end of 45 days of incubation, the amount of P extracted from that soil was the least (398 mg P kg^{-1} soil) as compared to the other soils.

The net percentages of plant-available P released from PR or PR mixed with organic acids and added to soils in relation to incubation time are shown in Figures 45-47. The means of duplicate samples are reported in the Appendix (Tables 29-34). The net percentage of the P released was calculated by subtracting the percentage of P released of the control treatments from the PR or PR-organic acid treatments. Thus, this percentage of P released does not include the available native P released by the organic acids from the soils. The Duncan multiple range test was used to compare the

Table 14. Phosphorus released at successive incubation time (days) in soils treated with monocalcium phosphate

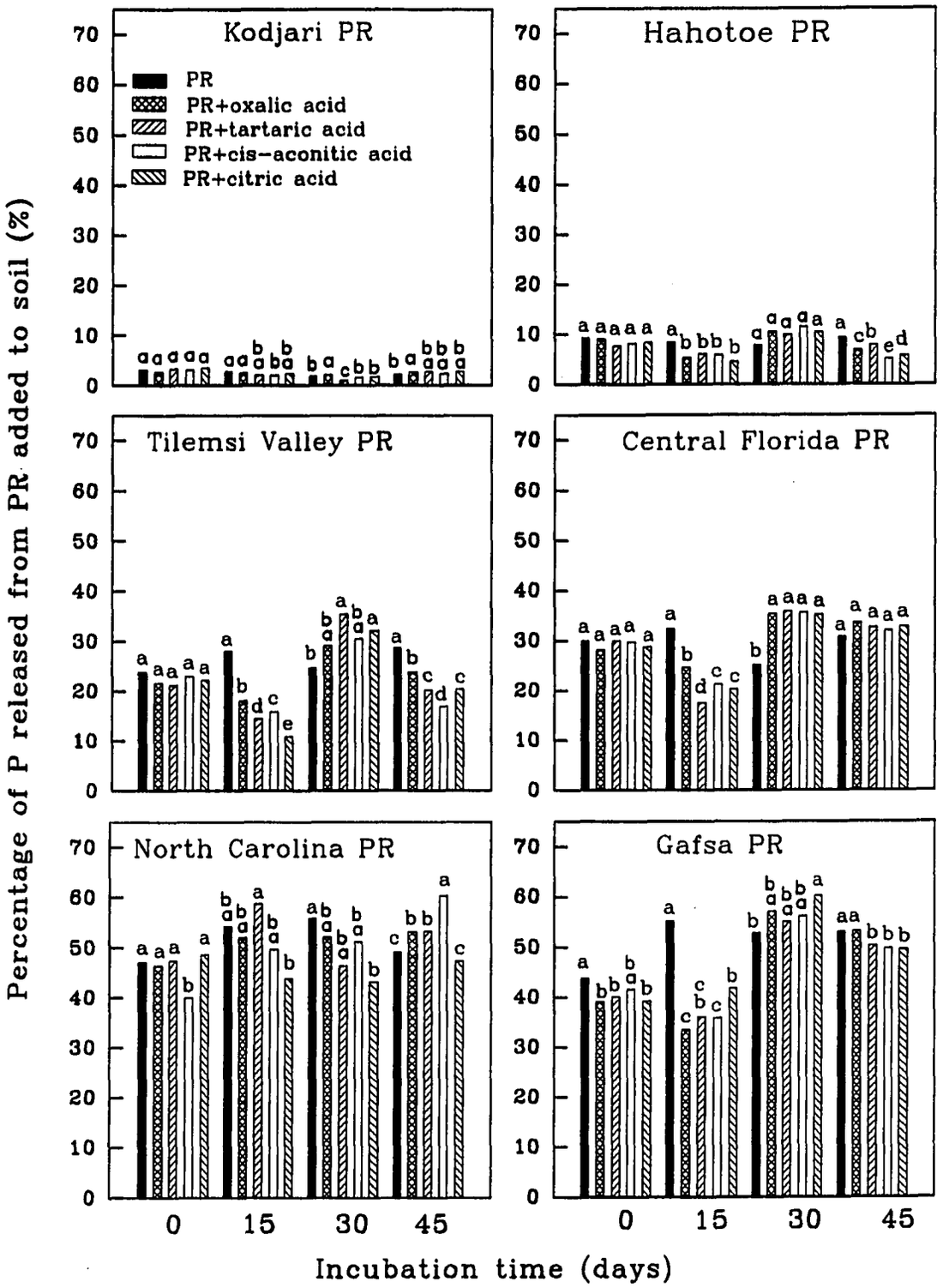
Soil	Incubation time (days)			
	0	15	30	45
Gosport	619	444	458	398
Clinton	558	440	412	426
Grundy	508	421	460	467

percentages of P released. The values obtained varied considerably from soil to soil and followed the order of Gosport soil > Grundy soil > Clinton soil. The percentages of P released varied also according to the reactivity of the rocks; the high reactive PRs (North Carolina and Gafsa) released more P than the medium reactive PRs (Tilemsi Valley and Central Florida), which, in turn, released more P than the low reactive PRs (Hahotoe and Kodjari). The poor performance of Hahotoe and Kodjari PRs added to Gosport soil is obvious; the percentage of P released did not exceed 3% from Kodjari PR and 12% from Hahotoe PR at any time during the incubation period, whereas up to 60% of P was released from North Carolina and Gafsa PRs. Increasing incubation time did not result in increasing the release of plant-available P in the Gosport soil. At zero incubation time, there was no significant difference among PRs

and their organic acid-treated counterparts ($p < 0.05$), with the exception of North Carolina PR treated with cis-aconitic acid, which was significantly less effective than PR alone and Gafsa PR treated with oxalic, tartaric, or citric acid, which were significantly less effective. The lack of response at time zero suggests that contact time is required for any chemical or biochemical reactions to take place in the soil mixed with PRs and organic acids. Increasing the incubation period from zero to 15 days corresponded, with a few exceptions (Hahotoe and North Carolina PRs), to a significantly low percentage of P released from organic acid treatments compared with PRs alone. Chauhan et al. (1981) observed a decrease in inorganic P release from 18.0 to 13.5 mg P kg^{-1} soil in two soils during the first five days of incubation following addition of cellulose without P application. In the experiments reported here, the added P source does not contain water-soluble P and consequently does not supply P to soils.

Although the increase in percentage P released was not always statistically significant ($p < 0.05$), it appears that in most cases 30 days of incubation corresponded to the greatest percentage P released. The largest increase in percentage P release from organic acid treatments compared with those obtained with PR alone averaged 10% for Central Florida PR (Figure 45). In the case of North Carolina PR, the rock alone was slightly better than its organic acid treatments even though the observed differences were not statistically significant ($p < 0.05$). Only at 45 days of incubation, most of the organic acid treatments of North Carolina PR were significantly better

Figure 45. Effect of incubation time and organic acids on the percentage of P released from various phosphate rocks added (200 mg P kg^{-1} soil) to Gosport soil


Kodjari PR
Hahotoe PR
Tilemsi Valley PR
Central Florida PR
North Carolina PR
Gafsa PR
PR
PR+oxalic acid
PR+tartaric acid
PR+cis-aconitic acid
PR+citric acid
Percentage of P released from PR added to soil (%)
Incubation time (days)
0
10
20
30
40
50
60
70
0
15
30
45

than the rock alone, with the exception of citric acid treatment which was as good as the rock alone. For most of the rocks, 45 days of incubation corresponded to a decrease in the percentage of plant-available P (Figure 45). In Clinton soil (Figure 46), all the organic acid treatments were significantly better than the PRs alone ($p < 0.05$) at 30 days of incubation, with the exception of the results obtained for Hahotoe PR where the rock alone was as effective as those with tartaric and citric acids. When the incubation time was increased to 45 days, only oxalic acid and cis-aconitic acid treatments were significantly better than North Carolina PR alone; for Gafsa PR the cis-aconitic and citric acid treatments were significantly better than the rock alone. Almost the same conclusion reached with Grundy soil, with the exception of that all the organic acid treatments released a significantly greater percentage of P than from North Carolina PR alone at zero incubation time (Figure 47).

These patterns in the dynamics of the percentage of plant-available P seem to be related to immobilization of P by soil microorganisms. Indeed, when readily available low-molecular-weight organic acids are added to soils, the acids are metabolized within a few hours or days. Part of the carbon (40-60%) may be transformed into microbial cells and products (Martin and Haider, 1986) and serves as an energy source for bacteria, whose number rapidly increases. Another part of the carbon may rapidly evolve as CO_2 and only a small portion of the organic acid therefore reacts with the PR to convert the latter into di- and monobasic phosphates with the net result of an increased availability of inorganic P. The released inorganic P is, however,

Figure 46. Effect of incubation time and organic acids on the percentage of P released from various phosphate rocks added (200 mg P kg^{-1} soil) to Clinton soil

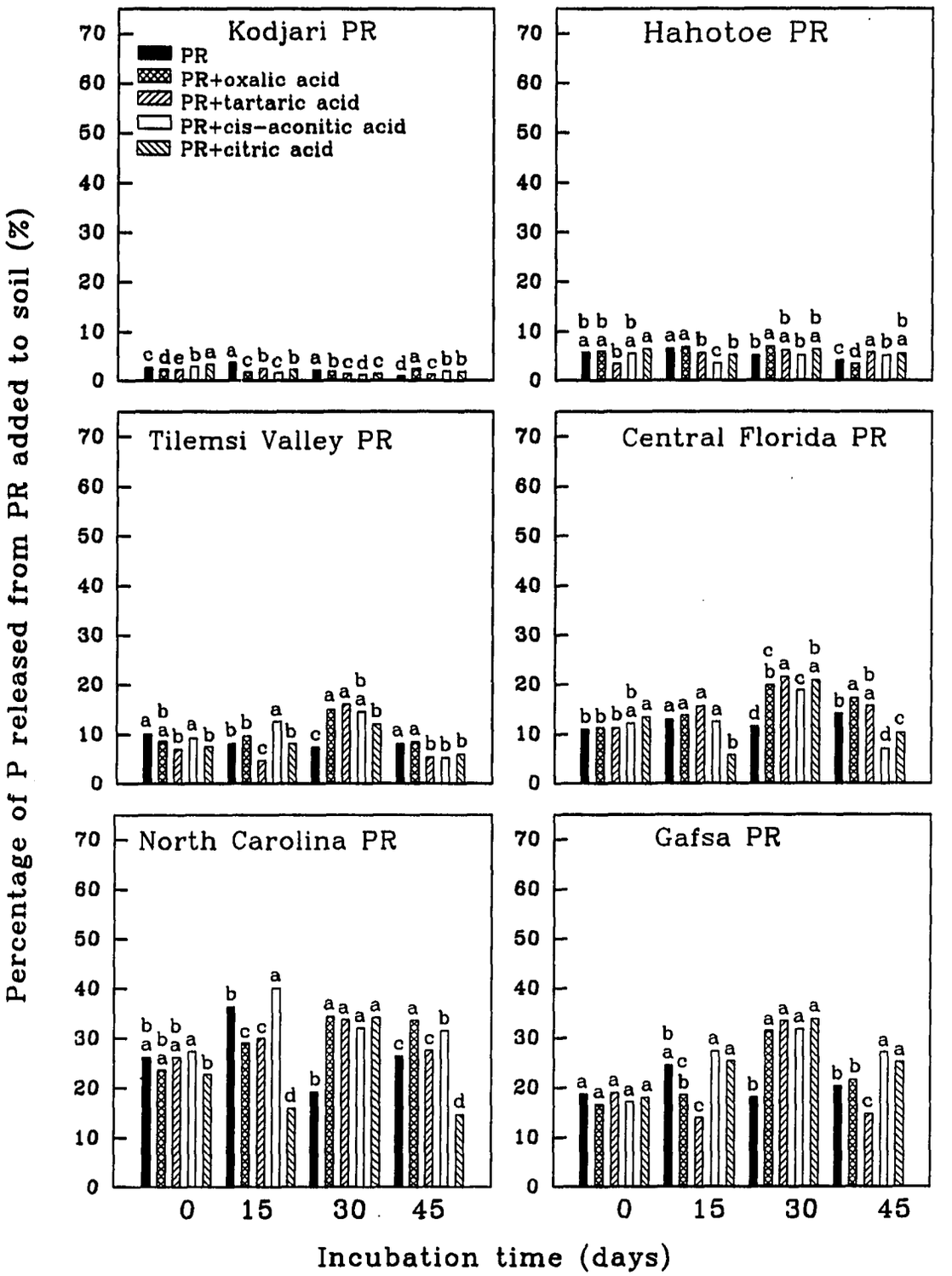
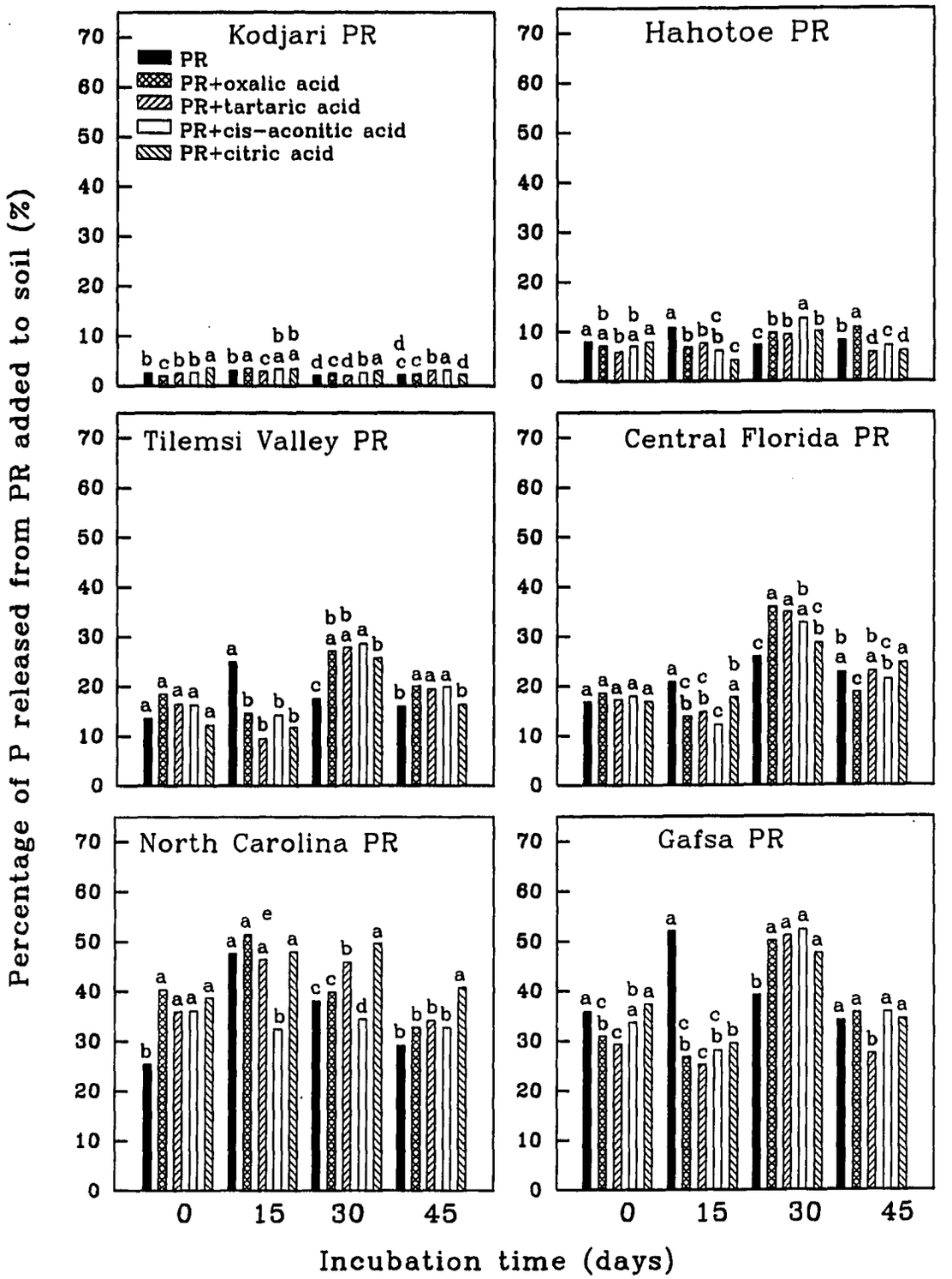

Kodjari PR
PR
PR+oxalic acid
PR+tartaric acid
PR+cis-aconitic acid
PR+citric acid
Hahotoe PR
Tilemsi Valley PR
Central Florida PR
North Carolina PR
Gafsa PR
Percentage of P released from PR added to soil (%)
Incubation time (days)
0
15
30
45
10
20
30
40
50
60
70

Figure 47. Effect of incubation time and organic acids on the percentage of P released from varoius phosphate rocks added (200 mg P kg^{-1} soil) to Grundy soil


Kodjari PR
PR
PR+oxalic acid
PR+tartaric acid
PR+cis-aconitic acid
PR+citric acid
Hahotoe PR
Tilemsi Valley PR
Central Florida PR
North Carolina PR
Gafsa PR
Percentage of P released from PR added to soil (%)
Incubation time (days)
0
15
30
45
10
20
30
40
50
60
70

subjected to immobilization process, which involves incorporation of P into microbial cells and explains the decrease in the percentage of P released at 15 days of incubation as compared with those at zero time (Figures 45-47). The variation in the amount of P immobilized from the different organic acid treatments would depend on the microbial growth as well as on the abiotic parameters. The significant decrease in the percentage of P released from some PR-organic acid treatments (up to 50%) suggests that increase in microbial abundance puts a great demand on phosphate supply. Consequently, if a PR is deficient in available P, microbial assimilation of this available P may depress crop yield. The immobilized P was eventually released 30 days after incubation for most PRs and 45 days of incubation from North Carolina PR, corresponding to the sharp increase in the percentage of plant-available P observed (Figure 45-47). Contrary to MCP treatments, which showed a systematic decrease in plant-available P with increasing incubation time, the treatments with organic acids containing several functional groups (OH and COOH) showed a peak in the extracted plant-available P at 30 or 45 days of incubation, suggesting that presence of organic acids in these treatments not only increased P availability from PRs, but also complexed Fe and Al components of the soils to reduce P sorption (Hue, 1991). In this study, none of the organic acid used seems to be consistently better than the others in terms of increasing plant-available P. However, oxalic acid and citric acids were selected for the greenhouse experiment because of their performance in previous experiments (Parts I and II), and also because they differ in number and type of functional groups. The results obtained under greenhouse conditions are reported in Part IV.

PART IV. EFFECT OF ORGANIC ACIDS ON THE PHYTOAVAILABILITY OF PHOSPHORUS IN PHOSPHATE ROCKS ADDED TO SOILS

INTRODUCTION

Although apatite is the common mineral found in phosphate rock, agronomic effectiveness of PRs varies widely according to their reactivity. In general, PRs can be divided into three groups of reactivity: (1) high reactive PRs, those PRs that may under suitable soil conditions be as good as triple superphosphate or single superphosphate; (2) medium reactive PRs, those that may in some cases release P in quantities sufficient enough to support plant growth, and (3) low reactive PRs, those which are not suitable for direct application because they do not release P for plant uptake. Some low reactive PRs can be used for processing water-soluble P fertilizers, whereas others cannot be used in the fertilizer industry because of their high Al and/or Fe oxide contents. The high cost of P fertilizers produced from PRs has limited the use of these fertilizers for crop production, especially in developing countries. The presence of indigenous phosphate deposits in some countries provides incentive for direct application or local chemical treatment at low cost to improve solubility of low reactive PRs. Such chemical treatment includes partial acidulation of PRs with sulfuric or phosphoric acid or compaction of PR with water-soluble P fertilizers (Kpomblekou et al., 1991). The use of organic acids that are produced in soil as microbial metabolites or plant exudates from dead or living cells represents a new perspective in phosphate rock research. Organic acids carry various functional groups that may play a significant role in PR dissolution. An effective acid in PR solubilization must dissociate and provide a sink for the calcium released from PR to insure constant PR dissolution.

Certain organic acids have been identified as very effective in soil mineral solubilization by providing protons and forming organo-complexes with Ca, Fe, and Al (Parts II and III). The hypothesis behind this work was that organic acids may complex Ca from PRs and cause release of P into the soil solution for plant uptake. Consequently, a greenhouse experiment was conducted to assess the phytoavailability of phosphorus in soils treated with phosphate rocks and organic acids.

MATERIALS AND METHODS

Soils

Surface samples (0-15 cm) of Gosport, Clinton, and Grundy soils used in Part III were selected for this study because they contained very low levels of plant-available P. The methods of analysis for the physical and chemical properties of these soils were described in the Materials and Methods section of Part III (Table 13).

Phosphate Rocks

Six phosphate rocks were selected for this work. These included two high reactive (North Carolina and Gafsa), two medium reactive (Tilemsi Valley and Central Florida), and two low reactive (Kodjari and Hahotoe) PRs. The chemical properties of these rocks are reported in Part I (Tables 2-4 and 6-7).

Organic Acids

Two organic acids (oxalic and citric) were selected for their outstanding performance during the laboratory P release experiments reported in Parts II and III. These acids were reagent-grade chemicals obtained from Fisher Scientific Co. (St. Louis, MO).

Procedures

The PR samples and the organic acids were ground separately to pass a 100-mesh (150 μm) sieve. A 200-g sample of the finely ground PR was thoroughly mixed

with an appropriate amount of organic acid of similar size to give 50 mmol acid kg-1 PR. To facilitate weighing of the fertilizer material, glass beads (Cataphote Division, Ferro Corp., Jackson, Mississippi) of < 100 mesh were added to the organic acid-PR mixture to make a total weight of 400 g. An appropriate amount of the fertilizer material thus obtained with or without organic acid was weighted out to give concentrations of 50, 100, 150, and 200 mg P kg^{-1} soil. Calcium phosphate (monobasic-primary-purified) was also mixed with glass beads in the ratio of 1:20 and weighted out to give the same rates of P as previously stated.

One kilogram of soil (on an oven-dry basis) was thoroughly mixed on a plastic sheet with 5 mL of a nutrient solution containing: K, Mg, Mn, Zn, Cu, B, and S (Table 15) as recommended by Allen et al. (1976) and 5 mL of urea ammonium nitrate solution to give 200 mg N pot^{-1}. A portion of the soil was transferred to a plastic pot (11.5 cm deep by 11 cm diameter) that was lined with double polyethylene bags to prevent free draining. The pot was gently tapped to allow the soil to settle down. The P fertilizer material was then applied evenly at the surface of the soil and covered with the other portion of the soil in such a way that the fertilizer material laid in the soil at 3 cm below the soil surface. Controls (without P but with organic acid, and/or glass beads) were included for each soil. After potting, the soils were covered with a plastic sheet to keep the soil moist. The experimental design was an incomplete factorial with a total number of observations of 267 per soil.

Table 15. Sources and amounts of nutrients applied to all pots before planting

Nutrient[a]	Compound	Amount Applied
K	K_2SO_4	133
Mg	$MgSO_4.7H_2O$	4.7
Mn	$MnSO_4.H_2O$	3.7
Zn	$ZnSO_4.H_2O$	4
Cu	$CuSO_4.5H_2O$	1.3
B	$Na_2B_4O_7.10H_2o$	0.5
N	$CO(NH_2)_2.NH_4.NO_3$	100
S	SO_4^{2-}	38.3

[a]All the nutrients were added as solutions.

Two days after potting, the soils were watered with deionized water to a gravimetric water content of 24%, and each pot was planted with three corn (Zea mays L.) seeds (R X 746) at 2 cm above the fertilizer zone and the pots were covered with a plastic sheet. One week after germination, the plants were thinned to one plant per pot. Following thinning, all the pots were weighed and the moisture was adjusted with deionized water to a potential between -0.05 to -0.1 MPa. All the treatments were randomized following thinning. The pots were watered daily and the moisture adjusted

every week by weighing all the pots. Two weeks after emergence, K deficiency symptoms appeared on all soils and severely on Clinton soil. A solution of KNO_3 was applied to give 70 and 25 mg K and N pot^{-1}, respectively. At 25 days after planting, an additional 75 mg N pot^{-1} was added to each pot as urea-ammonium nitrate. A week later, a solution of K_2SO_4 was added to give 32 mg S pot^{-1}. The temperature in the greenhouse during this experiment averaged 20°C±2°C. Supplemental lighting was provided by suspended overhead lights. These lights provided an additional 125 $\mu E/m^2/sec$ of light and were lit for 14 hours/day.

After 60 days, the plant in each pot was cut above ground, dried in a forced-air drying oven, model SG-350 (The Grieve Corporation, Round Lake, IL) at 65°C for 5 days, and weighed and ground in a cyclone mill to pass through a 16-mesh screen. Total P content of the dried tissue sample was determined by a modification of the method described by Sommers and Nelson (1972). In this modification, 0.2 g of oven-dried plant sample was treated with 3 mL of concentrated nitric acid in a digestion tube and allowed to stand overnight. The tube was then placed in a preheated aluminum digestion block and heated for 15 min at 100°C. The tube was removed and allowed to cool down prior to the addition of 3 mL of 70% perchloric acid. Digestion proceeded at 203°C for about 75 min (until the solution cleared). After the tube has cooled down, deionized water was added to make a volume of 75 mL. The P concentration in the digests was measured colorimetrically using the method of Murphy and Riley

(1962) after neutralization with 5 N NaOH using p-nitrophenol as an indicator. From the concentration of P in the acid digest and the weight of plant material analyzed, the percentage P in the plant tissue was calculated.

RESULTS AND DISCUSSION

Six phosphate rocks of various reactivity were either applied directly or mixed with oxalic acid or citric acid to three soils in Greenhouse pots to give 0, 50, 100, 150, and 200 mg P kg^{-1} soil with or without 50 mmol kg^{-1} PR of organic acid. A marked difference was observed in dry matter yields and the yields of P in corn top. Results obtained were analyzed using the General Linear Model (GLM) program of the Statistical Analysis Systems (SAS) package (SAS Institute Inc. Cary, N.C.). The Least significant differences (LSD) were calculated at $p < 0.05$ to compare the effects of the treatments.

For convenience, the results obtained will be presented under the following subheadings: Effect of phosphate rocks and monocalcium phosphate added to soils, effect of oxalic and citric acids on phosphate rocks added to soils, and relationships between dry matter yield and yield of P. The individual results obtained are summarized in the Appendix (Tables 35-37).

Effect of Phosphate Rocks and Monocalcium Phosphate Added to Soils

Plant growth response to the six phosphate rocks applied to the three soils are illustrated in Figures 48-53. The response curves obtained demonstrate considerable differences among the phosphate rock sources in their ability to supply plant-available P. These curves also indicate that dry matter and P yields produced from pots that received North Carolina and Gafsa PRs were greater than those produced from pots

that received other PRs. The trends of yield responses obtained on Gosport soil (Figures 48 and 51) were similar to those shown for Clinton soil (Figures 49 and 52) and Grundy soil (Figures 50 and 53). However, the dry matter and P yields produced on Gosport soil were higher than those produced on Grundy soil, which, in turn, were higher than those produced in Clinton soil.

Tilemsi Valley and Central Florida PRs were inferior to North Carolina and Gafsa, but definitively better than Kodjari and Hahotoe PRs (Figure 48 and 51). The average dry matter and P yields produced on Gosport soil were, respectively, 5.8 g and 6.3 mg for North Carolina PR, 4.9 g and 6.0 mg for Gafsa PR, 4.6 g and 5.5 mg for Tilemsi Valley PR, 4.6 g and 5.2 mg for Central Florida PR, 3.7 g and 3.9 mg for Hahotoe PR, and 2.1 g and 2.4 mg for Kodjari PR. In general, the order of dry matter and P-yield production was North Carolina PR $\geq$ Gafsa PR $>$ Tilemsi Valley PR $\geq$ Central Florida PR $>$ Hahotoe PR $\geq$ Kodjari PR. This ranking corresponded to the reactivity scale exhibited by these rocks in ammonium citrate (pH 3) and formic acid (2%) (Table 4, Part I). The least significant difference test performed for comparison of the dry matter and P yields produced at the P application rates and on each soil (Tables 16 and 17) confirmed that the observed differences were statistically significant.

A quadratic model was used to describe the relationship between the dry matter yield produced and application of monocalcium phosphate at rates of 0, 50, 100, 150, and 200 mg P pot^{-1} (Figure 54A and B) on Gosport and Clinton soils, whereas a linear

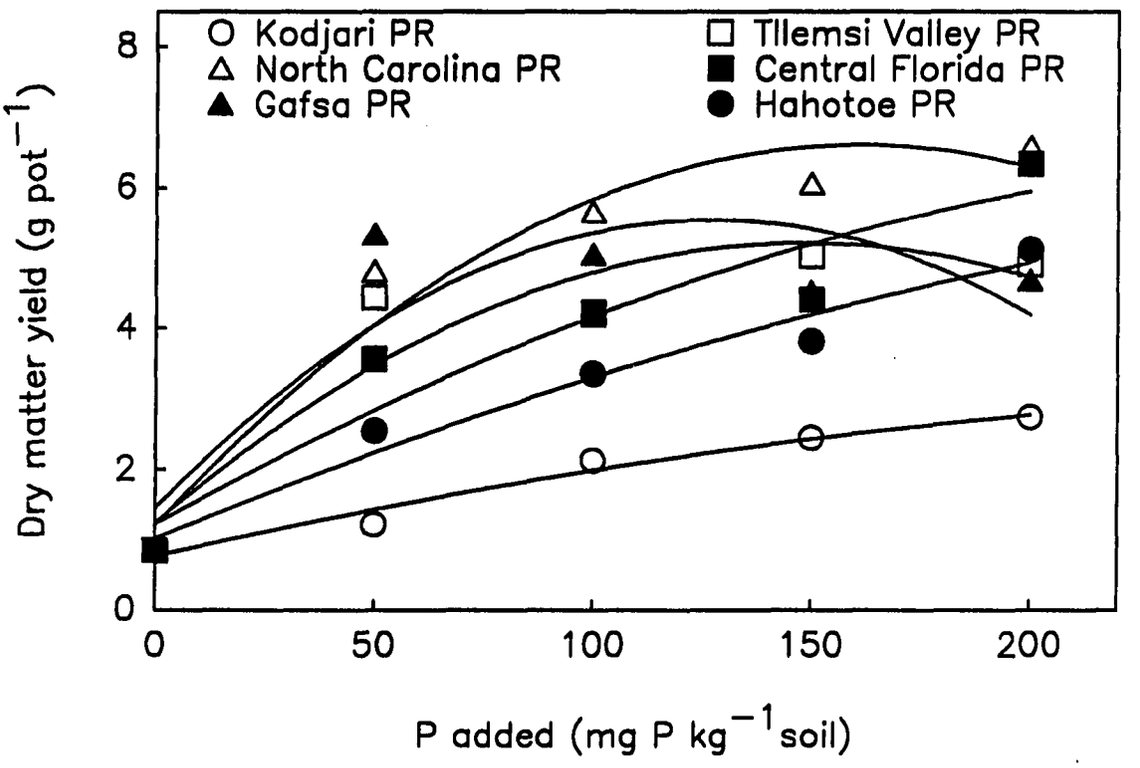


Figure 48. Effect of rates of P applied in various phosphate rocks on dry matter yields of corn tops produced on Gosport soil under greenhouse condition

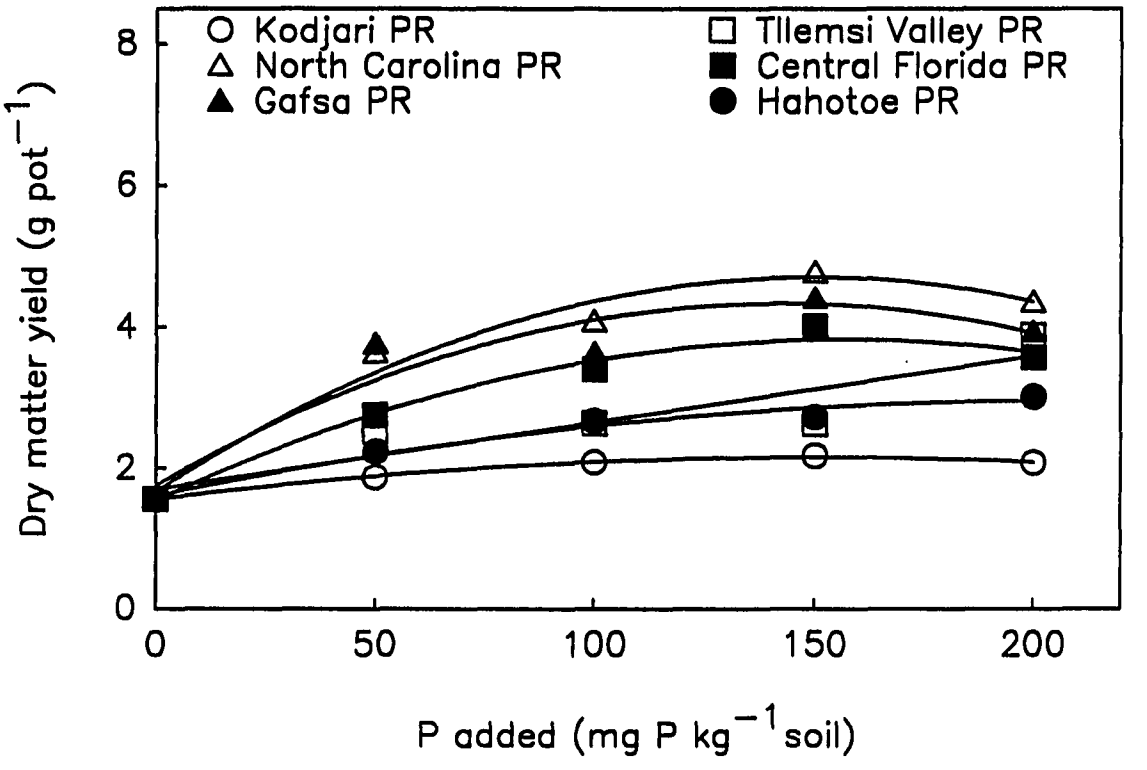


Figure 49. Effect of rates of P applied in various phosphate rocks on dry matter yields of corn tops produced on Clinton soil under greenhouse conditions

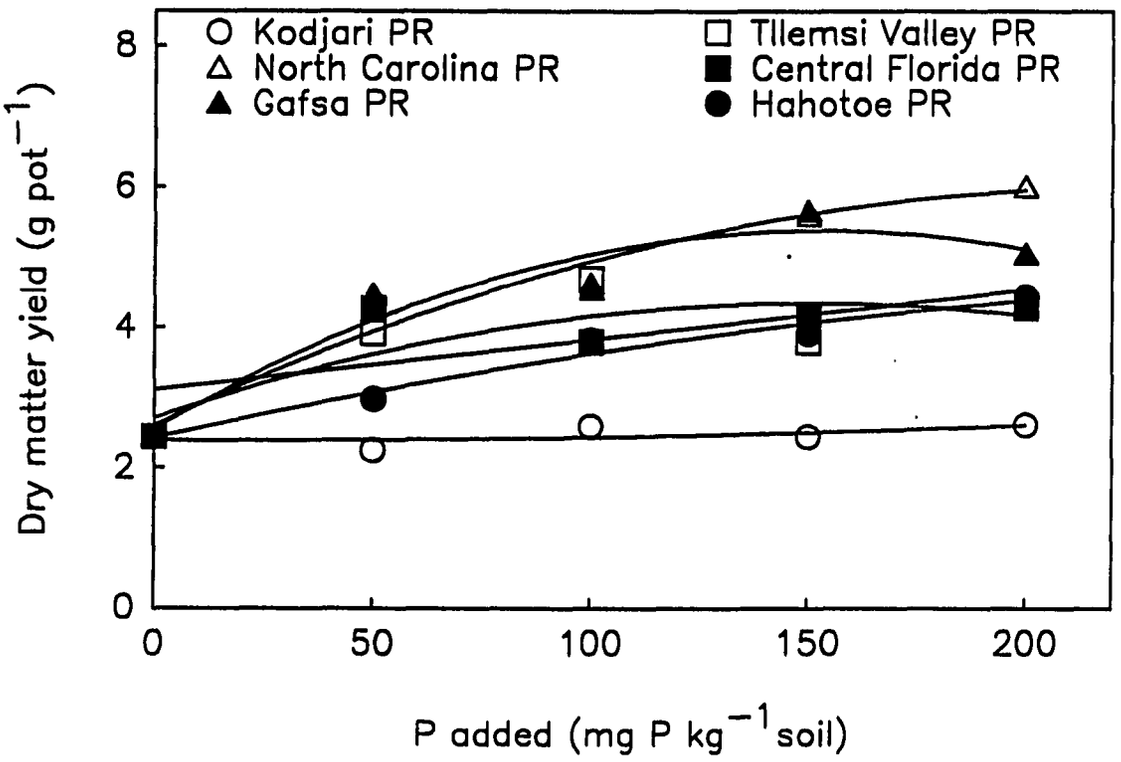


Figure 50. Effect of rates of P applied in various phosphate rocks on dry matter yields of corn tops produced on Grundy soil under greenhouse conditions

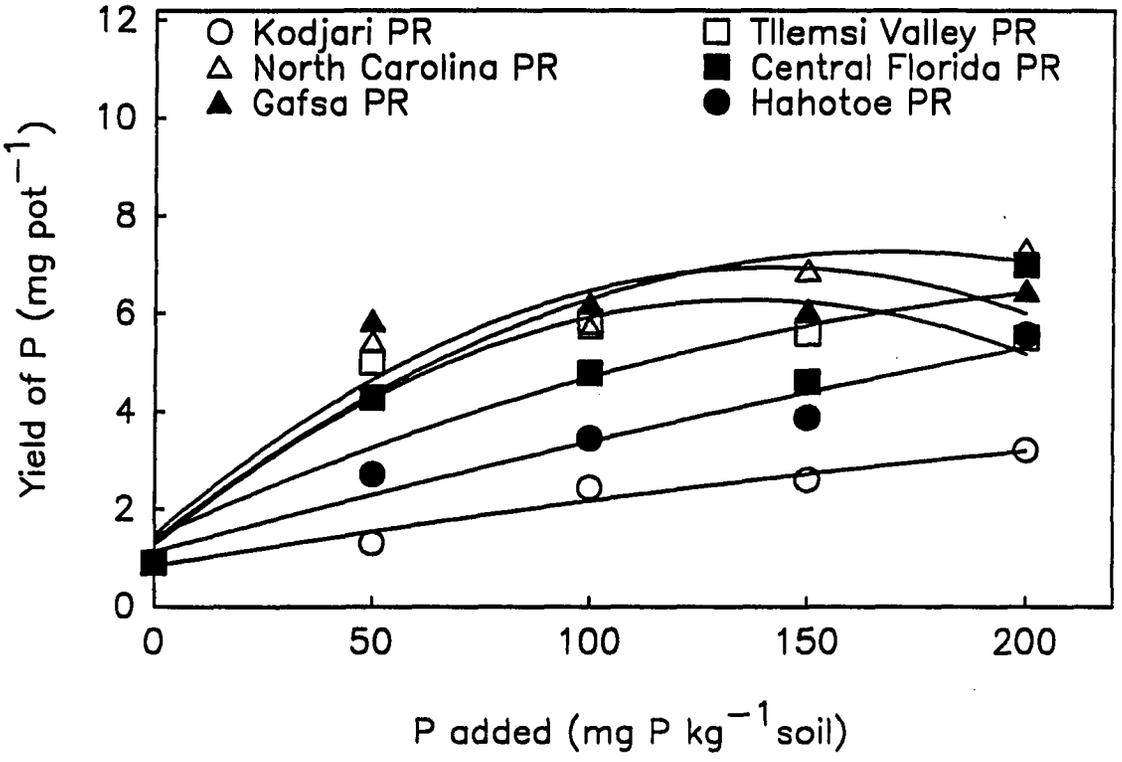


Figure 51. Effect of rates of P applied in various phosphate rocks on P yields of corn tops produced on Gosport soil under greenhouse conditions

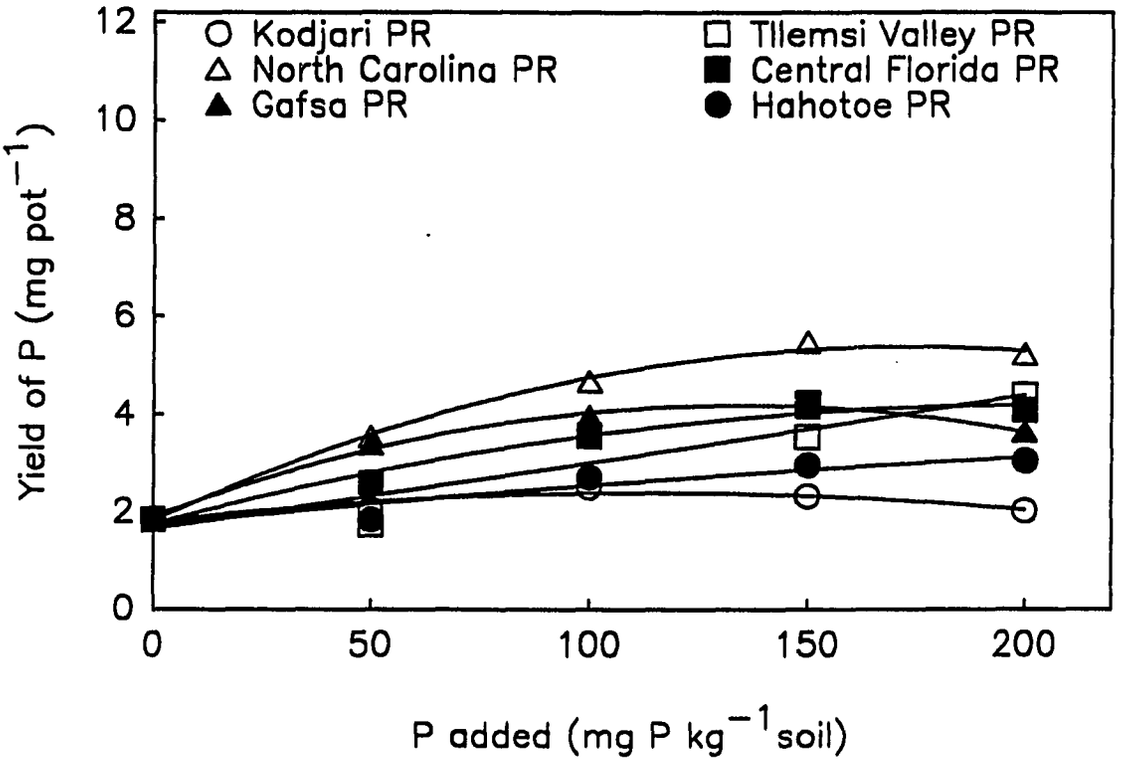


Figure 52. Effect of rates of P applied in various phosphate rocks on P yields of corn tops produced on Clinton soil under greenhouse conditions

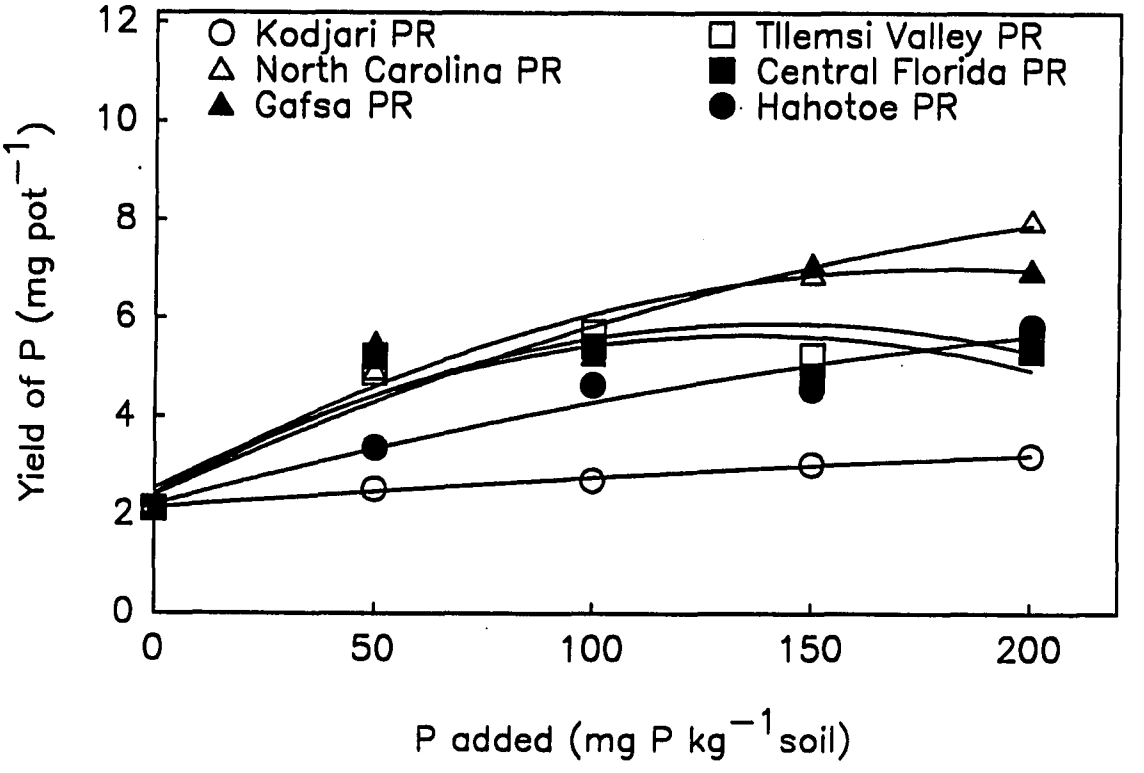


Figure 53. Effect of rates of P applied in various phosphate rocks on P yields of corn tops produced on Grundy soil under greenhouse conditions

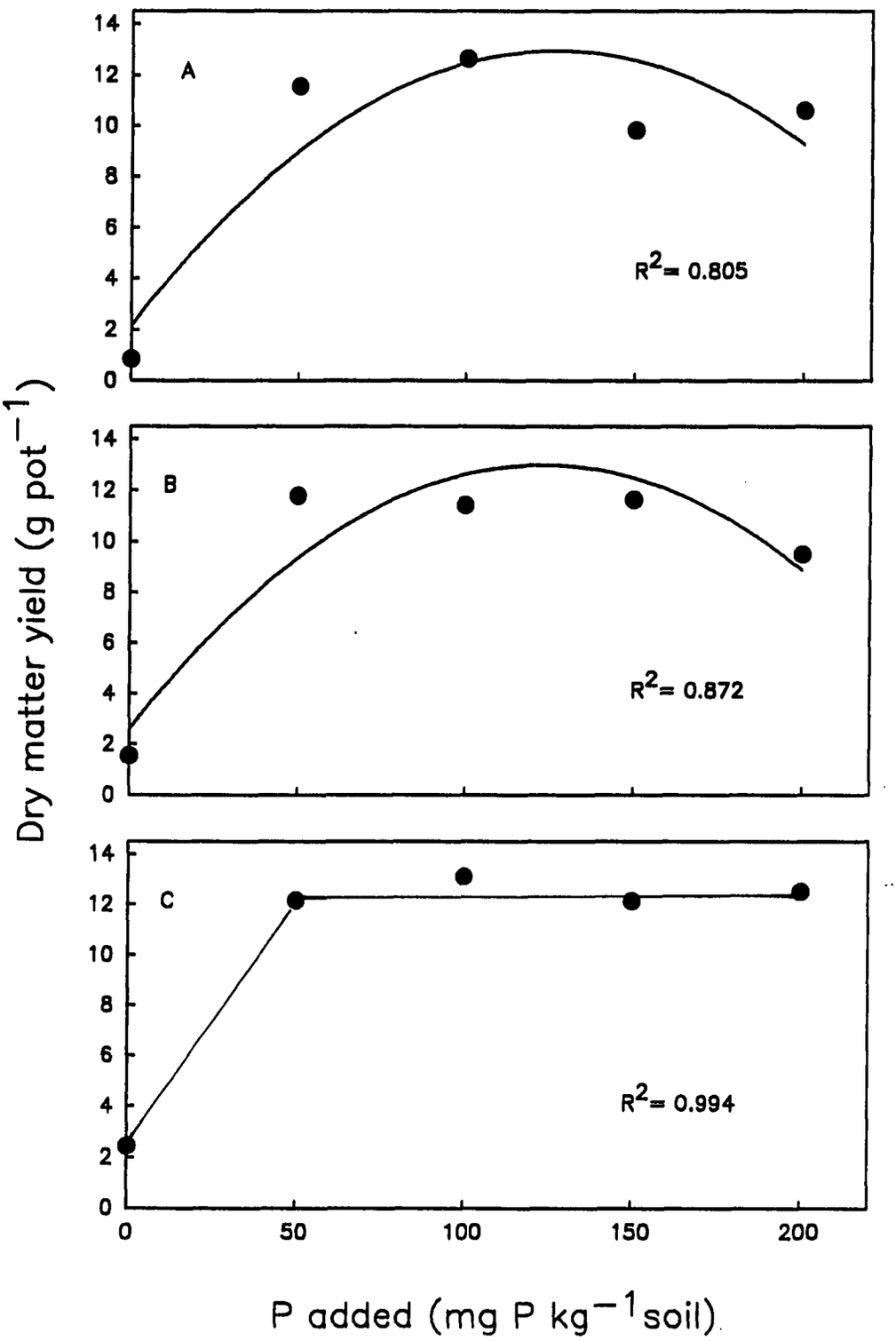
Table 16. Effect of sources and rates of phosphate rock (alone) on dry matter yield of corn tops produced on three soils

	Dry matter yield at rate of P applied (mg) per pot of soil specified											
	Gosport soil				Clinton soil				Grundy soil			
Phosphate rock	50	100	150	200	50	100	150	200	50	100	150	200
	g pot^{-1}											
Kodjari	1.2	2.1	2.4	2.7	1.9	2.1	2.2	2.1	2.2	2.6	2.4	2.6
North Carolina	4.8	5.6	6.1	6.6	3.6	4.1	4.8	4.4	4.4	4.6	5.6	6.0
Gafsa	5.3	5.1	4.5	4.7	3.8	3.6	4.4	3.9	4.5	4.5	5.7	5.0
Tilemsi Valley	4.4	4.2	5.0	4.9	2.5	2.6	2.6	3.9	3.9	4.7	3.8	4.3
Central Florida	3.4	4.2	4.4	6.3	2.8	3.4	4.0	3.6	4.3	3.8	4.2	4.3
Hahotoe	2.5	3.3	3.8	5.1	2.2	2.7	2.7	3.0	3.0	3.8	3.9	4.4
LSD $p < 0.05$	0.6	0.9	0.6	0.7	0.8	0.8	1.2	0.8	0.9	1.3	0.8	0.7

Table 17. Effect of sources and rates of phosphate rock (alone) on yield of corn tops produced on three soils

	Phosphorus yield at rate of P applied (mg) per pot of soil specified											
	Gosport soil				Clinton soil				Grundy soil			
Phosphate rock	50	100	150	200	50	100	150	200	50	100	150	200
	mg pot^{-1}											
Kodjari	1.3	2.4	2.6	3.2	2.0	2.5	2.3	2.0	2.5	2.7	3.0	3.2
North Carolina	5.4	5.7	6.9	7.3	3.5	4.7	5.5	5.2	4.9	5.4	6.9	8.0
Gafsa	5.8	6.2	6.1	6.5	3.4	4.0	4.1	3.6	5.5	5.2	7.1	7.0
Tilemsi Valley	5.0	5.8	5.6	5.5	1.8	3.6	3.5	4.4	4.9	5.7	5.2	5.6
Central Florida	4.2	4.8	4.6	7.0	2.6	3.6	4.2	4.1	5.2	5.4	4.8	5.3
Hahotoe	2.7	3.4	3.9	5.6	1.8	2.7	3.0	3.0	3.4	4.6	4.6	5.8
LSD $p <$	1.1	1.0	1.0	1.1	0.5	1.3	0.7	1.0	1.1	1.6	1.2	1.0

Figure 54. Effect of rates of monocalcium phosphate on dry matter yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions


A
B
C
R^2= 0.805
R^2= 0.872
R^2= 0.994
Dry matter yield (g pot^{-1})
P added (mg P kg^{-1}soil)
0
2
4
6
8
10
12
14
0
50
100
150
200

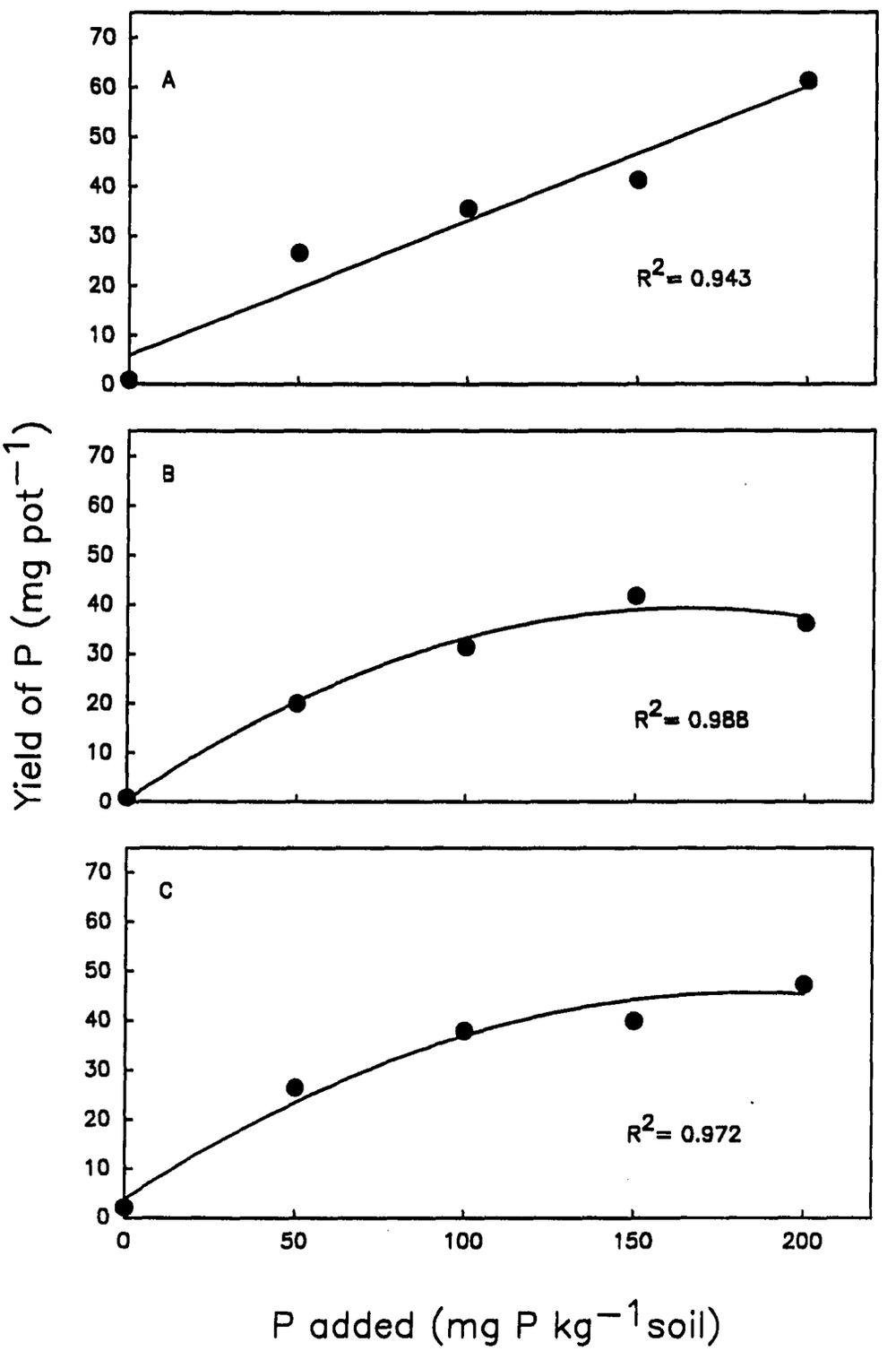
plus plateau was appropriate on Grundy soil (Figure 54C). A sharp rise in dry matter yield production was observed on Gosport and Clinton soils (Figure 54A and B) between 0 and 100 mg P application rates; further increases in P application rates decreased the dry matter yield production. On Grundy soil, application of 50 mg P pot^{-1} of fertilizer as MCP was enough to produce maximum dry matter yield (Figure 54C). Contrary to previous suggestions, only one of three P yield curves was an upward straight line, and the two others were curvilinear. It is assumed that application of monocalcium phosphate increased root growth, which, in turn, increased the volume of soil in contact with the rooting system. Subsequently, the amount of soil P absorbed by the plant from the soil increased linearly with increasing rate of P application (Figure 55A) on Gosport soil. On Clinton and Grundy soils, the trend of the curves suggest that the amounts of P absorbed from MCP are a linear function of the application rate, whereas the amounts of soil P decreased with increasing application rates (Figure 55B and C).

Effect of Oxalic and Citric Acids on Phosphate Rocks Added to Soils

Dry matter yield

Addition of organic acids to phosphate rocks did not always result in an increase in dry matter yield production. The effect of the organic acids varied according to PR, rate of P application, and soils used, suggesting differences in the mode of attack on the added organic acids. Mixing of the oxalic acid with Kodjari PR significantly reduced dry matter production at 100 and 150 mg P application rates, whereas mixing

Figure 55. Effect of rates of monocalcium phosphate on P yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions


A
B
C
R^2= 0.943
R^2= 0.988
R^2= 0.972
Yield of P (mg pot^{-1})
P added (mg P kg^{-1}soil)
0
10
20
30
40
50
60
70
0
50
100
150
200

this PR with citric acid did not affect dry matter yields (Table 18). On Clinton soil, application of Kodjari PR with citric acid significantly increased dry matter yield ($p < 0.05$) at P application rates of 50 and 200 mg pot^{-1}. On Grundy soil, however, application of Kodjari PR with citric acid was significantly better than Kodjari PR alone at 150 and 200 mg P rates (Table 18). The relationship between dry matter yield and P application rates of Kodjari PR is shown in Figure 56.

Mixing of Hahotoe PR with citric acid increased significantly the dry matter yield only at the 50 mg P application rate; at 200 mg P, the dry matter yield significantly decreased on Gosport soil (Table 19). Application of oxalic acid did not affect dry matter at the 50, 100, and 150 mg P application rates, but reduced significantly dry matter at 200 mg P. On Clinton and Grundy soils, the organic acids did not affect significantly the dry matter yield except at the 150 mg P application rate where Hahotoe + oxalic acid was significantly better than Hahotoe PR alone on Clinton soil (Table 19). The dry matter yield response curves showed increasing yields with increasing P application rates on all three soils (Figure 57); however, the dry matter production was greater on Gosport (Figure 57A) and Clinton (Figure 57B) than on Grundy (Figure 57C) soil.

The dry matter yields of corn produced at each application rate of Tilemsi Valley PR alone, Tilemsi Valley PR + oxalic acid or Tilemsi Valley PR + citric acid on all three soils are shown in Figure 58. On Gosport soil (Figure 58B) at low application rates (50 and 100 mg P), citric acid increased dry matter yield compared to that produced by Tilemsi Valley PR alone, but citric acid did not affect significantly dry

Table 18. Effect of oxalic acid and citric acid mixed with Kodjari PR on dry matter and P yields of corn tops produced on three soils

Soil / Phosphate rock	Dry matter and P yields at rate of P applied (mg) per pot							
	Dry matter yield				P yield			
	50	100	150	200	50	100	150	200
	--------g pot^{-1}----------				-------mg pot^{-1}---------			
Gosport								
Kodjari alone	1.2	2.1	2.4	2.7	1.3	2.4	2.6	3.2
Kodjari+oxalic acid	1.4	1.3	2.1	3.1	1.4	1.7	2.5	3.7
Kodjari+citric acid	1.2	2.0	2.3	2.8	1.3	2.4	2.8	2.8
LSD $p < 0.05$	0.2	0.4	0.3	0.6	0.4	0.6	0.4	0.7
Clinton								
Kodjari alone	1.8	2.1	2.2	2.1	2.0	2.5	2.3	2.0
Kodjari+oxalic acid	1.9	1.9	2.3	2.3	2.0	2.1	2.2	2.5
Kodjari+citric acid	2.2	2.1	2.7	2.7	1.8	2.1	2.6	2.9
LSD $p < 0.05$	0.3	0.4	0.6	0.6	0.5	0.4	0.4	0.7
Grundy								
Kodjari alone	2.2	2.6	2.4	2.6	2.5	2.7	3.0	3.2
Kodjari+oxalic acid	1.9	2.3	2.7	3.1	1.9	2.9	3.5	3.9
Kodjari+citric acid	2.0	2.7	3.2	3.7	2.1	2.8	3.9	4.6
LSD $p < 0.05$	0.7	0.8	0.8	0.9	0.7	0.8	0.8	1.1

Figure 56. Effectof Kodjari phosphate rock mixed with oxalic or citric acid on dry atter yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

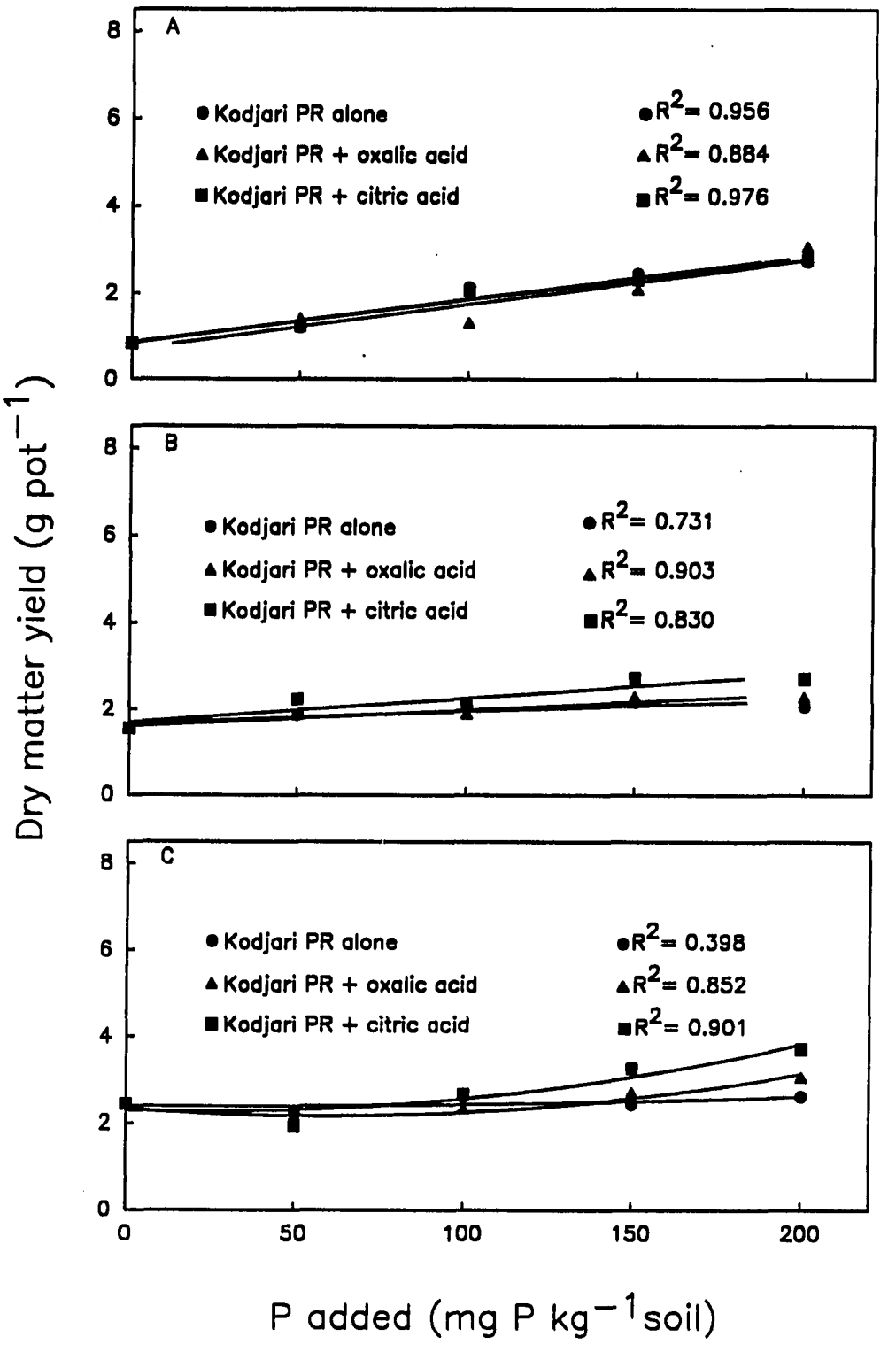

A
Kodjari PR alone
Kodjari PR + oxalic acid
Kodjari PR + citric acid
R2= 0.956
R2= 0.884
R2= 0.976
B
Kodjari PR alone
Kodjari PR + oxalic acid
Kodjari PR + citric acid
R2= 0.731
R2= 0.903
R2= 0.830
C
Kodjari PR alone
Kodjari PR + oxalic acid
Kodjari PR + citric acid
R2= 0.398
R2= 0.852
R2= 0.901
Dry matter yield (g pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
50
100
150
200

Table 19. Effect and rates of Hahotoe PR mixed with organic acids on dry matter and P yields of corn tops produced on three soils

Soil / Phosphate rock	Dry matter and P yields at rate of P applied (mg) per pot							
	Dry matter yield				P yield			
	50	100	150	200	50	100	150	200
	--------g pot^{-1}---------				-------mg pot^{-1}--------			
Gosport								
Hahotoe alone	2.5	3.3	3.8	5.1	2.7	3.4	3.9	5.6
Hahotoe+oxalic acid	2.3	2.8	4.4	4.6	2.9	2.8	3.7	5.5
Hahotoe+citric acid	3.4	4.0	3.7	3.8	4.3	5.1	4.2	4.2
LSD $p < 0.05$	0.5	1.3	0.7	0.4	0.9	1.4	1.3	0.9
Clinton								
Hahotoe alone	2.2	2.7	2.7	3.0	1.8	2.7	3.0	3.0
Hahotoe+oxalic acid	2.4	2.6	3.4	3.5	3.0	3.2	3.8	3.6
Hahotoe+citric acid	2.3	2.6	3.0	3.4	2.3	2.6	3.3	3.7
LSD $p < 0.05$	0.4	1.1	0.5	0.6	0.8	1.0	0.5	0.7
Grundy								
Hahotoe alone	3.0	3.8	3.9	4.4	3.4	4.6	4.6	5.8
Hahotoe+oxalic acid	3.0	3.1	4.0	4.6	3.6	4.3	5.1	6.3
Hahotoe+citric acid	3.0	3.5	3.5	4.2	3.7	4.3	4.0	5.6
LSD $p < 0.05$	1.2	0.7	0.9	0.8	0.8	1.2	1.5	0.6

Figure 57. Effect of Hahotoe phosphate rock mixed with oxalic or citric acid on dry matter yield of corn tops produced on Gosport (A), Clinton (B), and Grundy soils under greenhouse conditions

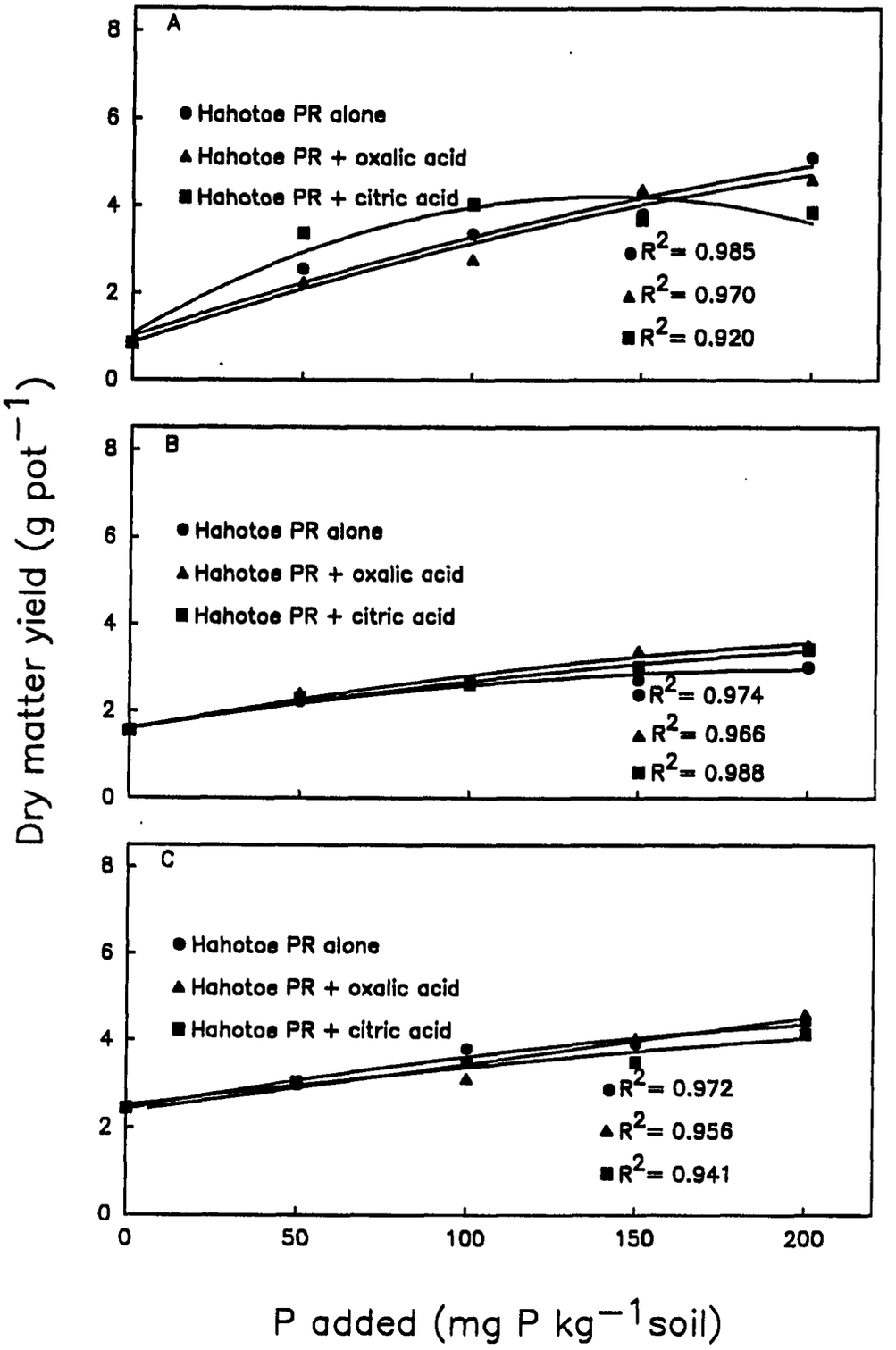
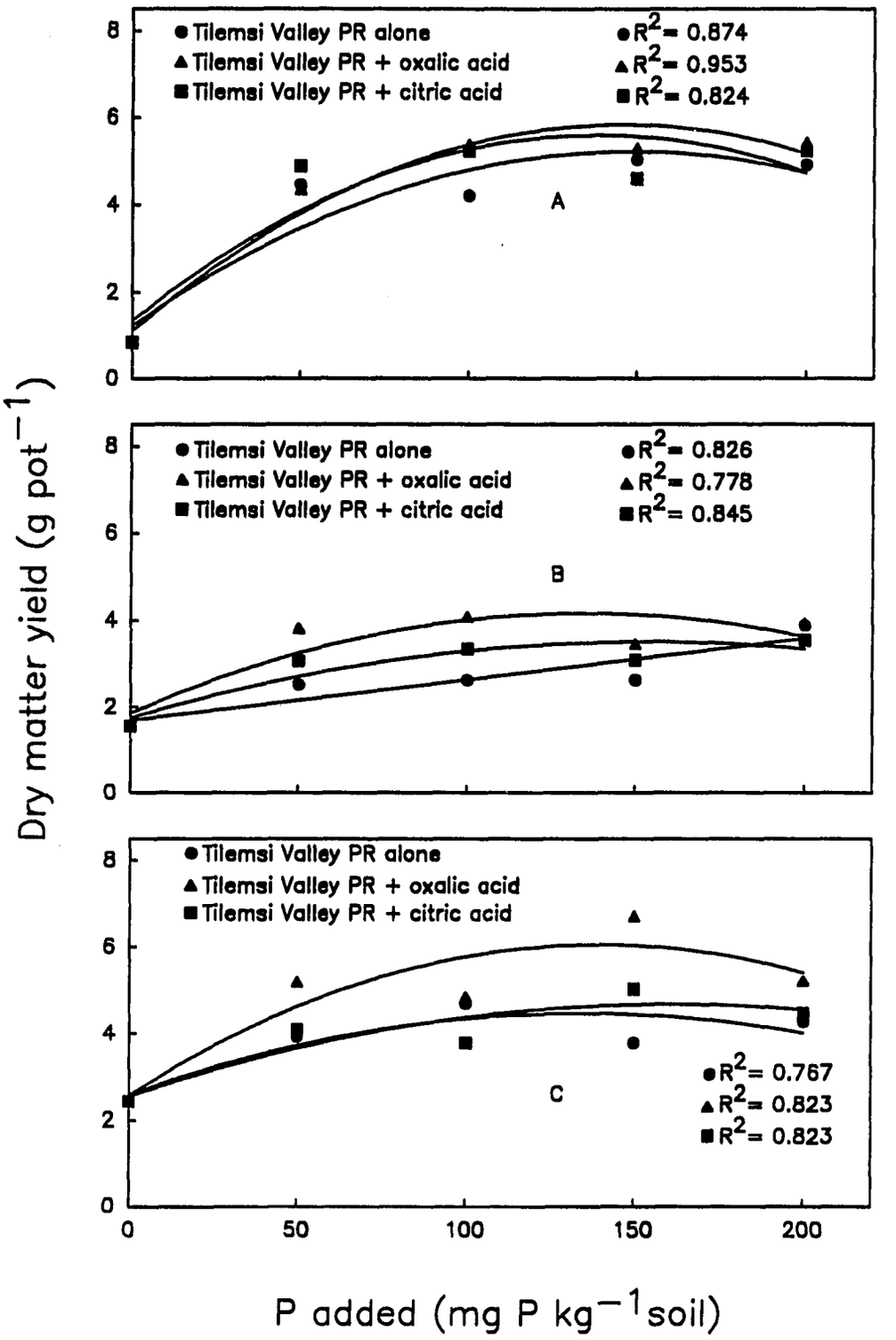

A
Hahotoe PR alone
Hahotoe PR + oxalic acid
Hahotoe PR + citric acid
R2= 0.985
R2= 0.970
R2= 0.920
B
Hahotoe PR alone
Hahotoe PR + oxalic acid
Hahotoe PR + citric acid
R2= 0.974
R2= 0.966
R2= 0.988
C
Hahotoe PR alone
Hahotoe PR + oxalic acid
Hahotoe PR + citric acid
R2= 0.972
R2= 0.956
R2= 0.941
Dry matter yield (g pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
0
50
100
150
200

Figure 58. Effect of Tilemsi Valley phosphate rock mixed with oxalic or citric acid on dry matter yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soil under greenhouse conditions


● Tilemsi Valley PR alone
▲ Tilemsi Valley PR + oxalic acid
■ Tilemsi Valley PR + citric acid
●R2= 0.874
▲R2= 0.953
■R2= 0.824
A
●R2= 0.826
▲R2= 0.778
■R2= 0.845
B
●R2= 0.767
▲R2= 0.823
■R2= 0.823
C
Dry matter yield (g pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
0
50
100
150
200

matter on Clinton (Figure 58B) and Grundy (Figure 58C) soils. Application of Tilemsi Valley PR + oxalic acid significantly increased corn dry matter yield at application rates of 50, 100, and 150 mg P on Clinton soil and at application rates of 50, 150, and 200 mg P on Grundy soil (Table 20). On Grundy soil, the increase was 1.3, 2.9, and 0.9 g/pot at 50, 150, and 200 mg P rates, respectively. Mixing of Central Florida PR with oxalic acid did not significantly affect the dry matter yield production on Gosport and Clinton soils (Figure 59). The increase, however, was significant on Grundy soil at 100, 150, and 200 mg P application rates (Figure 59C). Mixing of Central Florida PR with citric acid also increased dry matter yield, but the increase was significant only at the 100 mg P application rate on Gosport soil, at the 50 and 200 mg P application rates on Clinton, and at the 100 and 200 mg P application rates on Grundy soil (Table 21). The increase in dry matter yield observed at the same P application rates for the organic acid treatments compared to the control without acid suggests that additional P was released into the water-soluble P pool from PRs. There was no beneficial effect of organic acids at any rate when North Carolina PR was added to the soils (Figure 60); the dry matter yield was significantly reduced ($p < 0.05$) when citric acid was added to North Carolina PR at 200 mg P on Gosport and Grundy soils (Table 22).

Addition of organic acids to Gafsa PR increased significantly dry matter yield production only in few cases (Table 23). On Gosport soil (Figure 61A), oxalic acid increased the dry matter yield from 4.5 g to 6.2 g at the 150 mg P application rate and from 4.7 g to 5.3 g at the 200 mg P application rate. On Clinton soil (Figure 61B),

Table 20. Effect of oxalic acid and citric acid mixed with Tilemsi Valley PR on dry matter and P yields of corn tops produced on three soils

Soil / Phosphate rock	Dry matter and P yields at rate of P applied (mg) per pot							
	Dry matter yield				P yield			
	50	100	150	200	50	100	150	200
	--------g pot^{-1}----------				-------mg pot^{-1}---------			
Gosport								
Tilemsi Valley alone	4.4	4.2	5.0	4.9	5.0	5.8	5.6	5.5
Tilemsi Valley+oxalic acid	4.3	5.4	5.3	5.4	5.0	6.4	5.7	7.5
Tilemsi Valley+citric acid	4.9	5.2	4.6	5.2	6.0	6.5	5.6	5.6
LSD $p < 0.05$	0.4	0.9	0.4	0.7	1.3	1.4	1.7	0.8
Clinton								
Tilemsi Valley alone	2.5	2.6	2.6	3.9	1.8	3.6	3.5	4.4
Tilemsi Valley+oxalic acid	3.8	4.1	3.5	3.9	4.4	4.7	4.1	5.1
Tilemsi Valley+citric acid	3.1	3.4	3.1	3.5	3.9	3.7	3.1	4.3
LSD $p < 0.05$	0.7	1.1	0.6	0.9	0.6	1.1	0.8	0.9
Grundy								
Tilemsi Valley alone	3.9	4.7	3.8	4.3	4.9	5.7	5.2	5.6
Tilemsi Valley+oxalic acid	5.2	4.8	6.7	5.2	5.5	5.4	8.5	7.1
Tilemsi Valley+citric acid	4.1	3.8	5.0	4.5	4.5	5.2	6.3	6.1
LSD $p < 0.05$	0.7	1.6	1.0	0.5	0.9	1.4	0.8	1.6

Figure 59. Effect of Central Florida phosphate rock mixed with oxalic or citric acid on dry matter yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

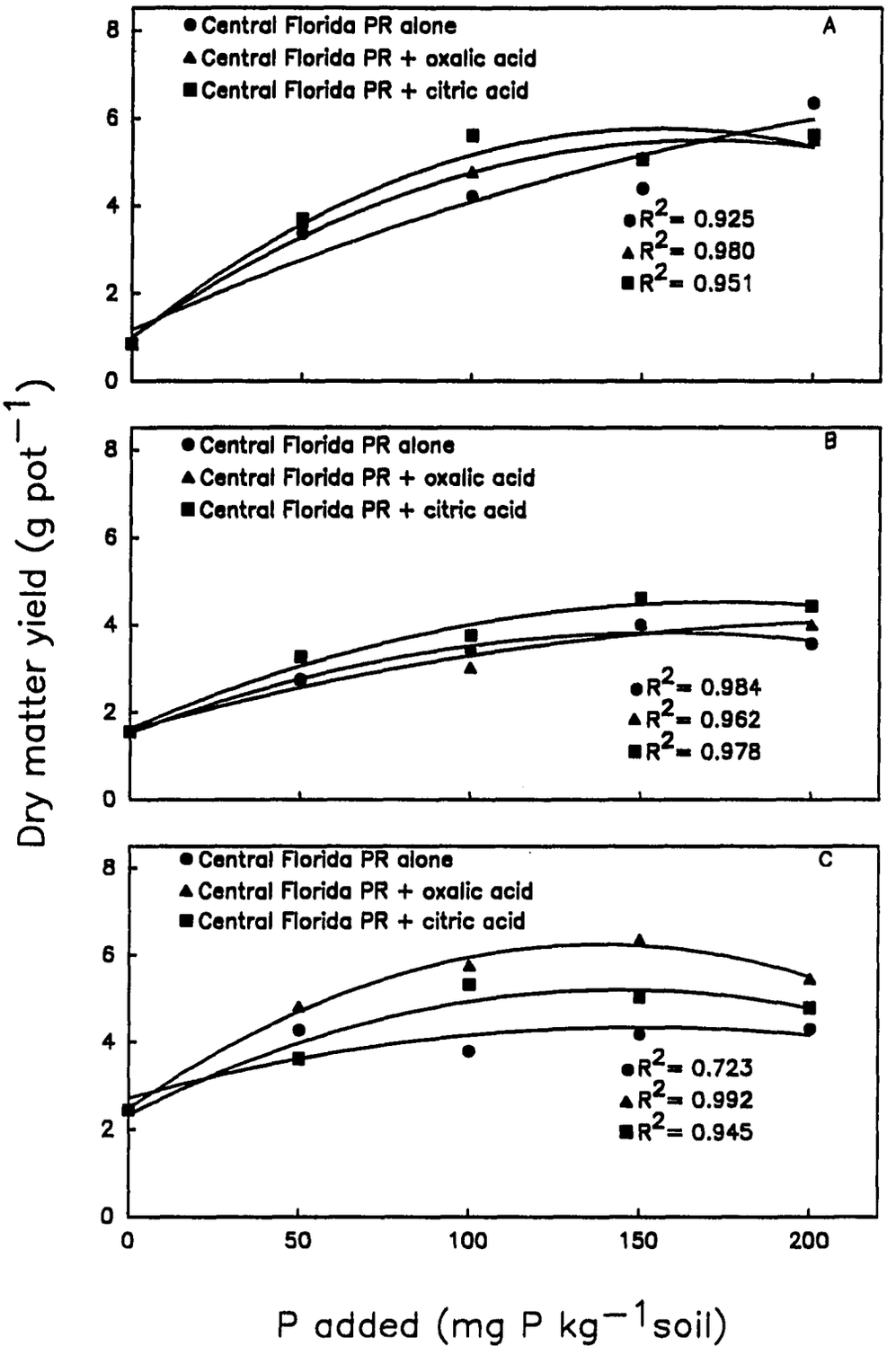

● Central Florida PR alone
▲ Central Florida PR + oxalic acid
■ Central Florida PR + citric acid
A
●R2= 0.925
▲R2= 0.980
■R2= 0.951
B
●R2= 0.984
▲R2= 0.962
■R2= 0.978
C
●R2= 0.723
▲R2= 0.992
■R2= 0.945
Dry matter yield (g pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
50
100
150
200

Table 21. Effect of oxalic acid and citric acid mixed with Central Florida PR on dry matter and P yields of corn tops produced on three soils

Soil Phosphate rock	Dry matter and P yields at rate of P applied (mg) per pot							
	Dry matter yield				P yield			
	50	100	150	200	50	100	150	200
	--------g pot^{-1}---------				-------mg pot^{-1}--------			
Gosport								
Central Florida alone	3.4	4.2	4.4	6.3	4.3	4.8	4.6	7.0
Central Florida+oxalic acid	3.6	4.8	5.1	5.5	5.0	5.0	5.6	6.1
Central Florida+citric acid	3.7	5.6	5.1	5.6	4.1	6.3	6.2	7.0
LSD $p < 0.05$	0.6	1.0	1.1	1.2	0.9	1.5	1.4	1.0
Clinton								
Central Florida alone	2.8	3.4	4.0	3.6	2.6	3.6	4.2	4.1
Central Florida+oxalic acid	2.7	3.0	4.0	4.0	3.1	3.8	5.0	5.4
Central Florida+citric acid	3.3	3.8	4.4	4.4	3.5	4.6	5.0	5.0
LSD $p < 0.05$	0.4	0.6	0.7	0.7	0.4	1.0	0.6	1.0
Grundy								
Central Florida alone	4.3	3.8	4.2	4.3	5.2	5.4	4.8	5.3
Central Florida+oxalic acid	4.8	5.8	6.4	5.4	5.9	7.5	8.0	7.3
Central Florida+citric acid	3.6	5.3	5.0	4.8	4.4	6.4	6.4	7.1
LSD $p < 0.05$	0.8	1.4	0.9	0.4	1.1	1.8	1.2	0.8

Figure 60. Effect of North Carolina phosphate rock mixed with oxalic or citric acid on dry matter yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

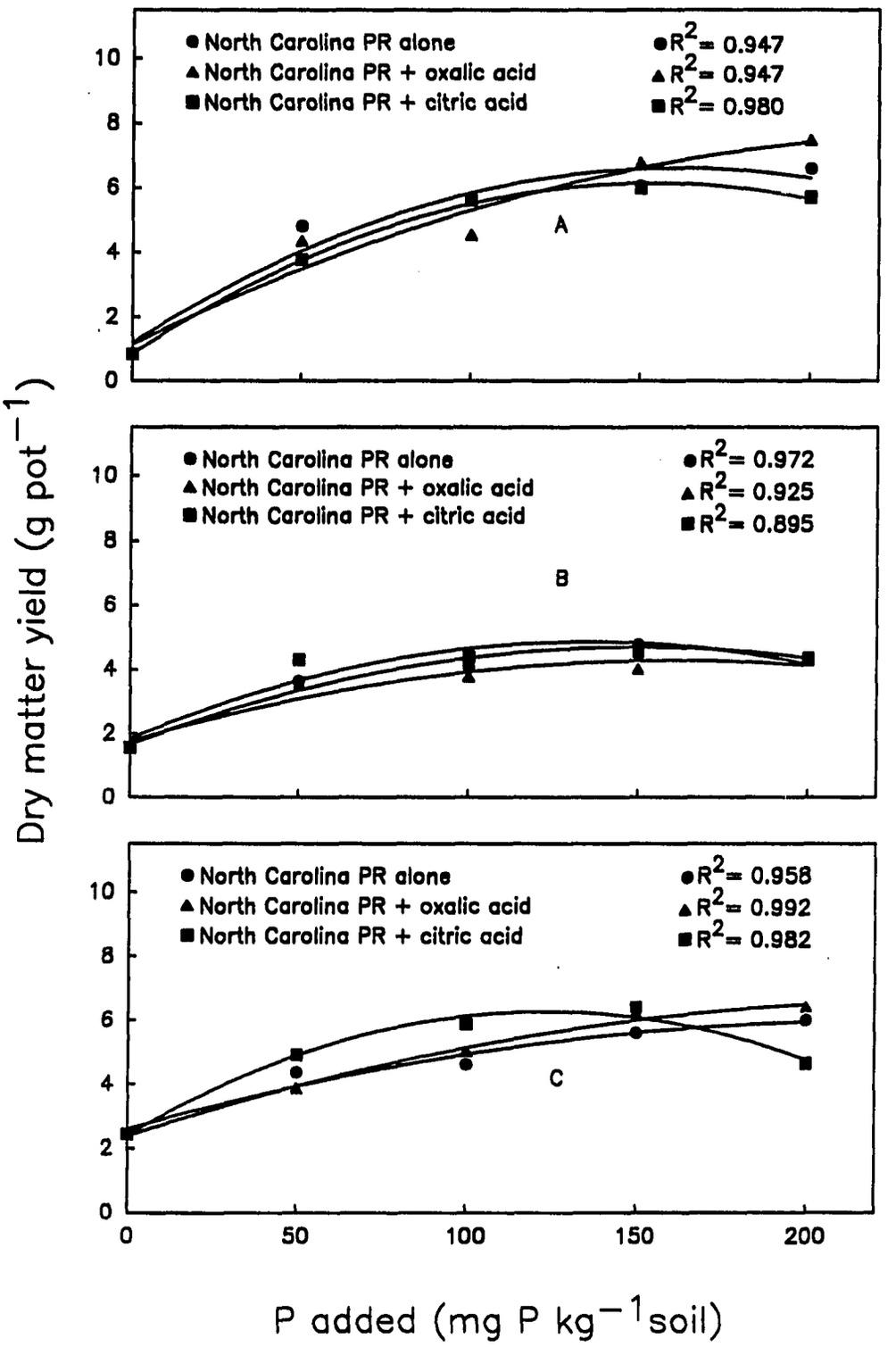

● North Carolina PR alone
▲ North Carolina PR + oxalic acid
■ North Carolina PR + citric acid
●R2= 0.947
▲R2= 0.947
■R2= 0.980
A
●R2= 0.972
▲R2= 0.925
■R2= 0.895
B
●R2= 0.958
▲R2= 0.992
■R2= 0.982
C
Dry matter yield (g pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
10
50
100
150
200

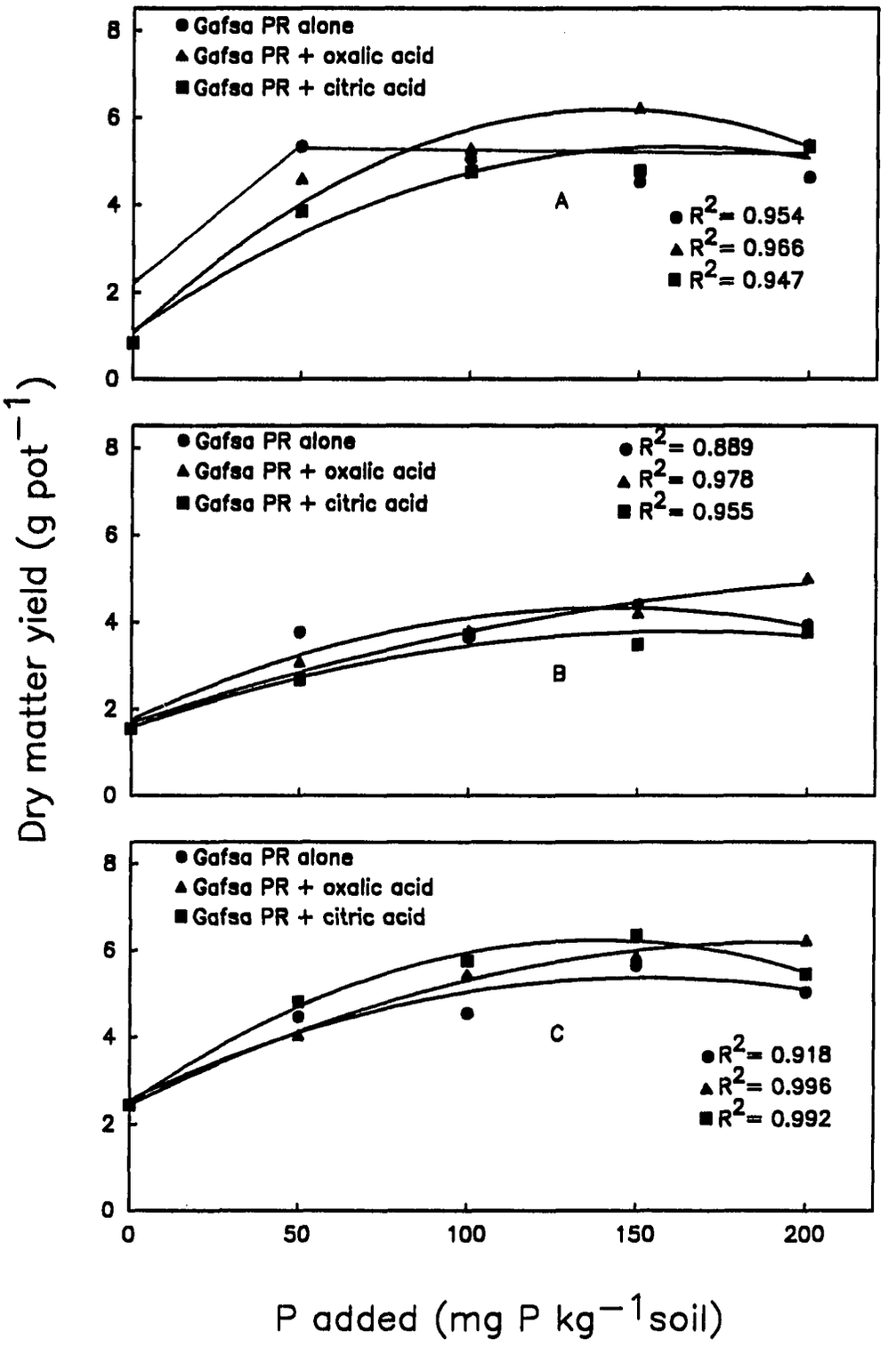
Table 22. Effect of oxalic acid and citric acid mixed with North Carolina PR on dry matter and P yields of corn tops produced on three soils

Soil Phosphate rock	Dry matter and P yields at rate of P applied (mg) per pot							
	Dry matter yield				P yield			
	50	100	150	200	50	100	150	200
	--------g pot^{-1}---------				-------mg pot^{-1}--------			
Gosport								
North Carolina alone	4.8	5.6	6.0	6.6	5.4	5.7	6.9	7.3
North Carolina+oxalic acid	4.4	4.5	6.8	7.5	5.2	5.8	7.1	10.1
North Carolina+citric acid	3.8	5.6	6.0	5.7	3.9	6.0	5.0	6.8
LSD $p < 0.05$	0.9	1.5	0.7	0.8	1.2	1.3	0.6	1.4
Clinton								
North Carolina alone	3.6	4.1	4.8	4.4	3.5	4.7	5.5	5.2
North Carolina+oxalic acid	3.5	3.8	4.0	4.3	4.1	4.2	4.4	4.9
North Carolina+citric acid	4.3	4.4	4.5	4.3	4.9	4.7	5.2	4.8
LSD $p < 0.05$	0.7	0.5	1.0	1.2	0.4	0.7	0.8	0.9
Grundy								
North Carolina alone	4.4	4.6	5.6	6.0	4.9	5.4	6.9	8.0
North Carolina+oxalic acid	3.9	5.0	6.2	6.4	5.6	5.4	8.8	9.1
North Carolina+citric acid	4.9	5.9	6.4	4.6	6.4	7.7	7.3	6.7
LSD $p < 0.05$	0.9	1.9	1.8	1.1	1.0	1.7	1.5	1.6

Table 23. Effect of oxalic acid and citric acid mixed with Gafsa PR on dry matter and P yields of corn tops produced on three soils

Soil Phosphate rock	Dry matter and P yields at rate of P applied (mg) per pot							
	Dry matter yield				P yield			
	50	100	150	200	50	100	150	200
	--------g pot^{-1}----------				-------mg pot^{-1}---------			
Gosport								
Gafsa alone	5.3	5.0	4.5	4.7	5.8	6.2	6.1	6.5
Gafsa+oxalic acid	4.6	5.3	6.2	5.4	5.9	6.5	7.6	6.8
Gafsa+citric acid	3.8	4.8	4.8	5.3	4.5	6.4	5.9	7.2
LSD $p < 0.05$	0.7	0.6	0.8	0.5	0.9	0.8	1.3	1.4
Clinton								
Gafsa alone	3.8	3.6	4.4	3.9	3.4	4.0	4.1	3.6
Gafsa+oxalic acid	3.1	3.8	4.2	5.0	3.9	3.7	4.6	6.3
Gafsa+citric acid	2.7	3.7	3.5	3.8	3.1	4.9	4.6	4.9
LSD $p < 0.05$	0.6	1.1	1.4	0.8	0.8	1.9	0.6	1.0
Grundy								
Gafsa alone	4.4	4.5	5.7	5.0	5.5	5.2	7.1	7.0
Gafsa+oxalic acid	4.1	5.5	5.9	6.2	5.6	6.4	7.6	7.4
Gafsa+citric acid	3.8	5.0	5.2	4.6	5.2	7.0	6.6	6.6
LSD $p < 0.05$	1.4	1.6	0.8	1.3	1.3	1.2	1.0	1.6

Figure 61. Effect of Gafsa phosphate rock mixed with oxalic or citric acid on dry matter yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions


● Gafsa PR alone
▲ Gafsa PR + oxalic acid
■ Gafsa PR + citric acid
A
● R^2= 0.954
▲ R^2= 0.966
■ R^2= 0.947
B
● R^2= 0.889
▲ R^2= 0.978
■ R^2= 0.955
C
● R^2= 0.918
▲ R^2= 0.996
■ R^2= 0.992
Dry matter yield (g pot^{-1})
P added (mg P kg^{-1}soil)
0
2
4
6
8
50
100
150
200

the increase was significant ($p < 0.05$) only at the 200 mg P application rate. On the other hand, citric acid increased dry matter yield only on Gosport soil from 4.7 g to 5.3 g at the 200 mg P application rate (Table 23). A quadratic model was adequate to describe the relationship between dry matter yield and P application rates on the soils and for all treatments (Figure 61), except for Gafsa PR alone where a linear+ plateau was used (Figure 61A).

The effectiveness of the organic acids in increasing dry matter yield seems to be related to the reactivity scale of the phosphate rocks. In general, no positive effect was observed when organic acids were mixed with low reactive PRs (Kodjari and Hahotoe) or with high reactive PRs (North Carolina and Gafsa). Medium reactive PRs (Tilemsi Valley and Central Florida), however, showed a potential for organic acids to increase dry matter yield production. Several factors may explain the lack of response to organic acid application, to the decrease of dry matter yield, or to the increase in dry matter yield production. Addition of readily available low-molecular-weight organic acids to soil is usually followed by a rapid metabolism of the acids in a few hours or days (Martin and Haider, 1986). In such conditions, where the acids are decomposed into $C0_2$ and H_20, there cannot be any complexation of metal cations in the phosphate rock or any acidifying effect of the acids on the surrounding environment, which would favor a release of inorganic P into soil solution. Razzaghe and Robert (1979) pointed out that organic acid dissociation and the release of protons is an important process precursor to complexing reactions that take place between ligands and certain elements

that are present in solution. In some cases, addition of the organic acids to PRs showed a significant decrease in dry matter yield, reflecting growth depression by PR + organic acid treatment relative to the controls (PRs alone). Although this was not a consistent pattern, the significant decrease in dry matter yield following addition of oxalic acid to Kodjari PR was observed on Gosport soil at the 100 and 150 mg P application rate (Table 18), of oxalic acid to Hahotoe at the 200 mg P rate on Gosport soil (Table 19), of citric acid to North Carolina at the 200 mg P application rate on Gosport and Grundy soil and at 50 mg P on Gosport soil (Table 22), and on Clinton at the 50 mg P application rate when Gafsa PR was mixed with either oxalic or citric acids (Table 23). This net decrease may be attributed to a competition for P between the corn plant and a growing microbial population at an earlier stage of growth. Indeed, after addition of organic acid to soils, under favorable microenvironmental conditions (moisture and pH), the acids may persist in soils and microorganisms may use the carbon of the acids for biosynthesis of new cells or use it as an energy source. The net result is an increase in the microbial pollution which competes for carbohydrates. Chauhan et al. (1981) estimated an increase in microbial C by a factor of 1.5 to 2.0 following addition of cellulose to two soils. They also noticed a decrease in inorganic P from 18.0 ug to 13.2 mg kg^{-1} soil during the first five days of incubation followed by a slower decrease over a period of nine months after cellulose addition to soils without P application. This situation is similar to that found in this study, because phosphate rocks do not contain water-soluble P and only a small amount of P

would be released for microbial needs and plant uptake. In addition to the competition for C, there would be a competition for P between the plant and the microorganisms. Similar conclusions were reached by Bethlenfalvay et al. (1982) when colonization by VAM fungi inhibited plant growth. Addition of organic acids to PRs may also influence availability of P and consequently affect dry matter yield production in a positive manner. Organic acids serve a specific function in making P from PR available for plant uptake by complexing polyvalent cations in the PR and releasing P into solution. The released P promoted growth of corn plant roots, which, in turn, explored a larger soil volume and absorbed more P necessary for increasing dry matter yield.

Yield of P

The yield of P in corn tops was calculated from the dry matter yield and percentage of P in the harvested corn tops and is presented in Tables 18-23. These tables show that, with the exception of a few treatments, there was no significant difference between the control and the organic acid treatments when Kodjari or Hahotoe PR was used (Table 18 and 19). The same observation is true for North Carolina and Gafsa PRs (Tables 22 and 23). On Clinton and Grundy soils, however, addition of organic acid to Tilemsi Valley or Central Florida PR (Table 20 and 21) increased P yield relative to the control (PR alone) even though the increase was not always statistically significant ($p < 0.05$). The largest increase (4.5 mg pot^{-1}) relative to the control (without organic acid) was observed on Gosport soil (Table 22) when

North Carolina PR was mixed with oxalic acid at 200 mg P pot^{-1}. This increase in P uptake by the corn plant was partly due to an increase in percentage total P accumulated in the corn top. In the case of North Carolina PR, the total P in plant increased from 0.111% for the rock alone to 0.135% for the rock mixed with oxalic acid and added to Gosport soil (Appendix, Tables 35-37). The regression lines for all treatments on all soils showed an increase in P uptake with increasing P fertilization (Figures 62-67). The relationship between yield of P and P added was linear only in a few cases and curvilinear in the majority of cases suggesting that curves of yield cannot be only ascending straight lines.

The average increase in P yield that resulted from application of increasing P rates when PR was mixed with organic acid varied considerably; it was as low as 0.4 mg P pot^{-1} for Tilemsi Valley + citric acid on Clinton soil (Table 20) to as high as 4.9 mg P pot^{-1} for North Carolina PR + oxalic acid on Gosport soil (Table 22). Regardless of the source of PR used, the yield of P obtained on Clinton soil tended to be lower than that obtained on Gosport or Grundy soils of similar treatments. The effect of sources and of PRs mixed with organic acids on dry matter and P yields is shown in Table 38-41 (Appendix).

The relationship between the dry matter yield and yield of P of corn tops grown on Gosport, Clinton and Grundy soils are shown, respectively, in Figures 68-70. In these figures, the means of each level of P for the six PRs are plotted against nutrient uptake; each point represents the results of one PR. A plot of this type allows for a

Figure 62. Effect of Kodjari phosphate rock mixed with oxalic or citric acid on P yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

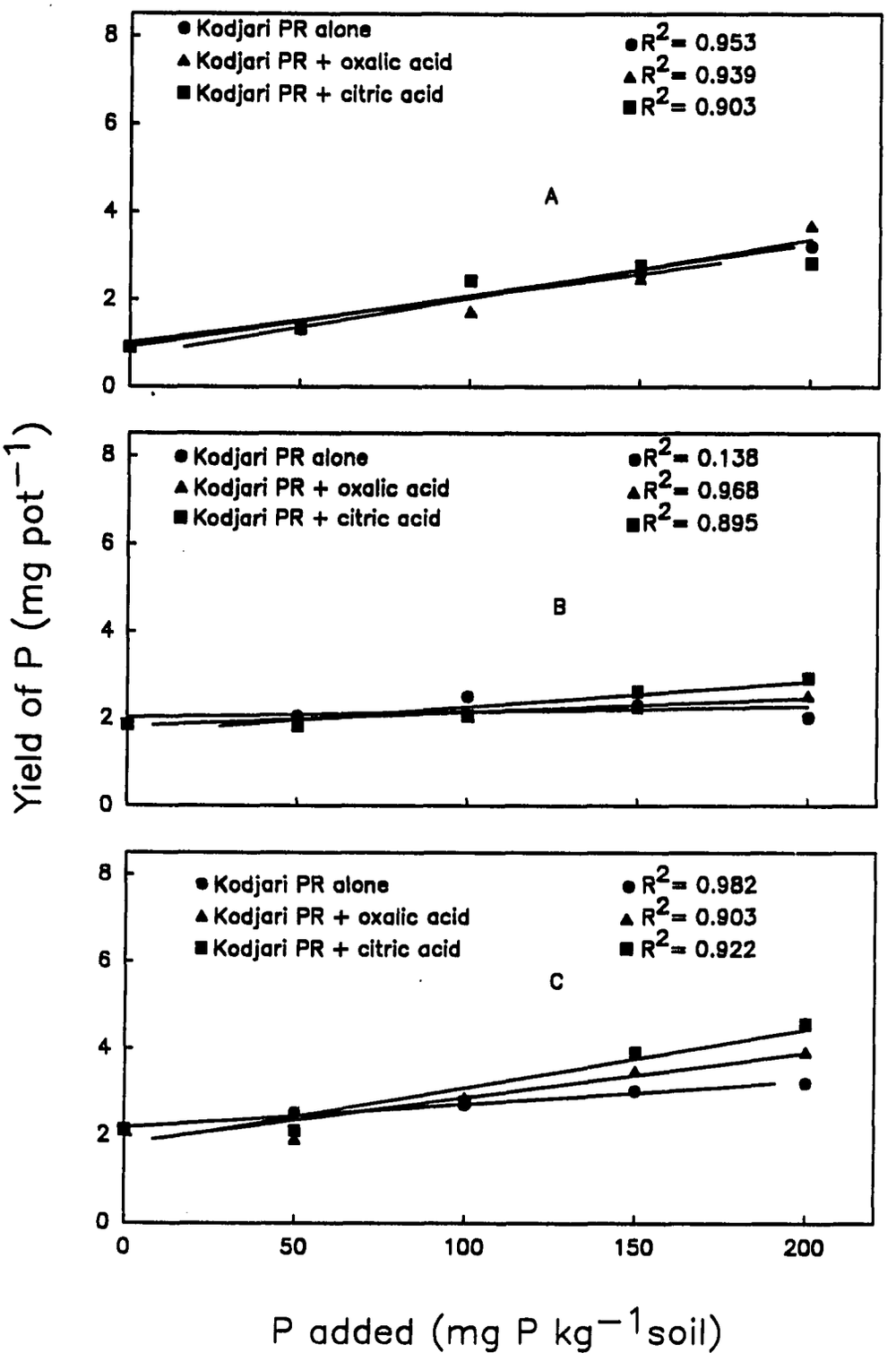

● Kodjari PR alone
▲ Kodjari PR + oxalic acid
■ Kodjari PR + citric acid
●R2= 0.953
▲R2= 0.939
■R2= 0.903
A
●R2= 0.138
▲R2= 0.968
■R2= 0.895
B
●R2= 0.982
▲R2= 0.903
■R2= 0.922
C
Yield of P (mg pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
50
100
150
200

Figure 63. Effect of Hahotoe phosphate rock mixed with oxalic or citric acid on P yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

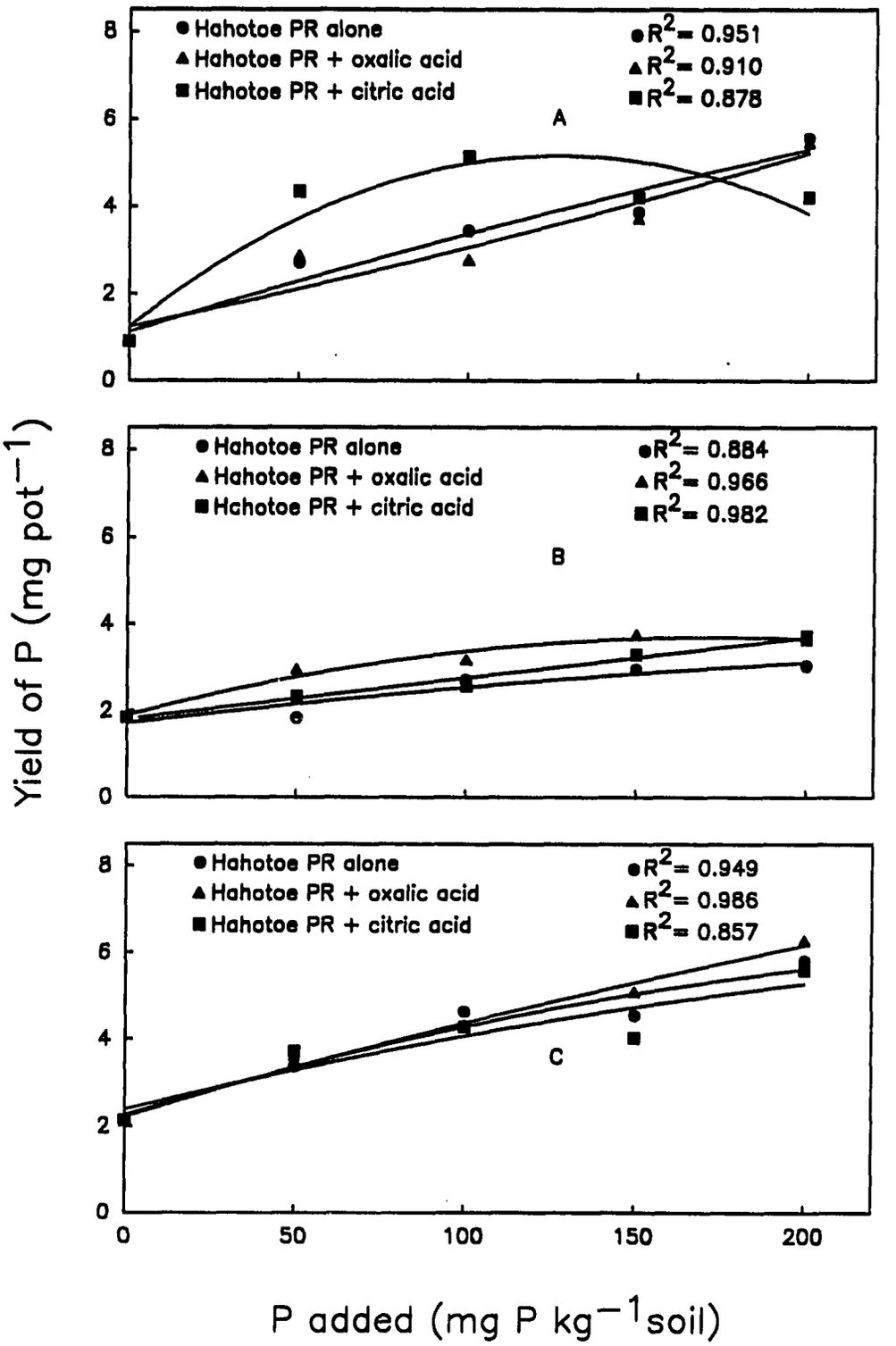

● Hahotoe PR alone
▲ Hahotoe PR + oxalic acid
■ Hahotoe PR + citric acid
●R2= 0.951
▲R2= 0.910
■R2= 0.878
A
●R2= 0.884
▲R2= 0.966
■R2= 0.982
B
●R2= 0.949
▲R2= 0.986
■R2= 0.857
C
Yield of P (mg pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
0
50
100
150
200

Figure 64. Effect of Tilemsi Valley phosphate rock mixed with oxalic or citric acid on P yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

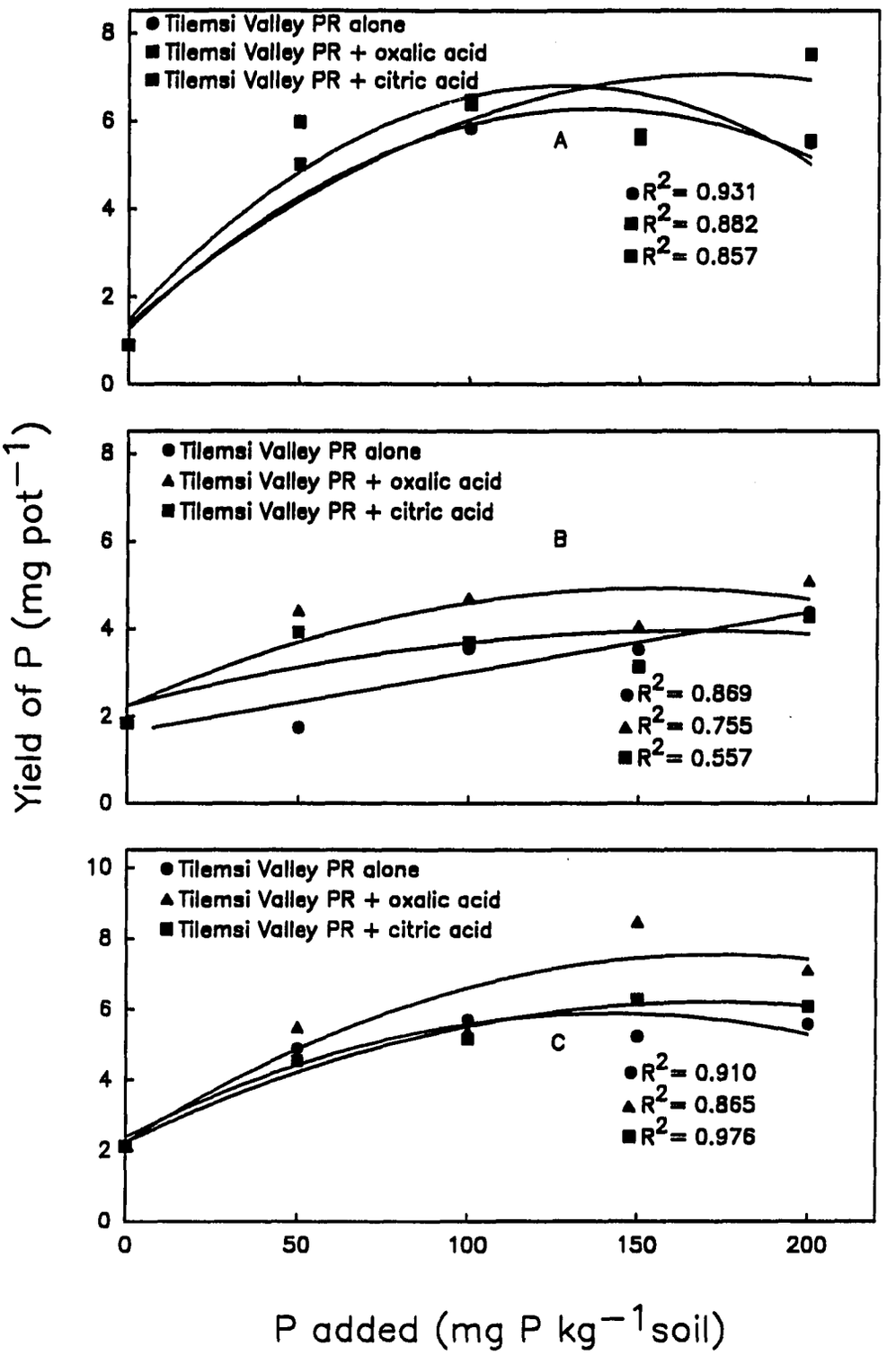

● Tilemsi Valley PR alone
■ Tilemsi Valley PR + oxalic acid
■ Tilemsi Valley PR + citric acid
A
●R2= 0.931
■R2= 0.882
■R2= 0.857
● Tilemsi Valley PR alone
▲ Tilemsi Valley PR + oxalic acid
■ Tilemsi Valley PR + citric acid
B
●R2= 0.869
▲R2= 0.755
■R2= 0.557
● Tilemsi Valley PR alone
▲ Tilemsi Valley PR + oxalic acid
■ Tilemsi Valley PR + citric acid
C
●R2= 0.910
▲R2= 0.865
■R2= 0.976
Yield of P (mg pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
10
0
50
100
150
200

Figure 65. Effect of Central Florida phosphate rock mixed with oxalic or citric acid on P yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

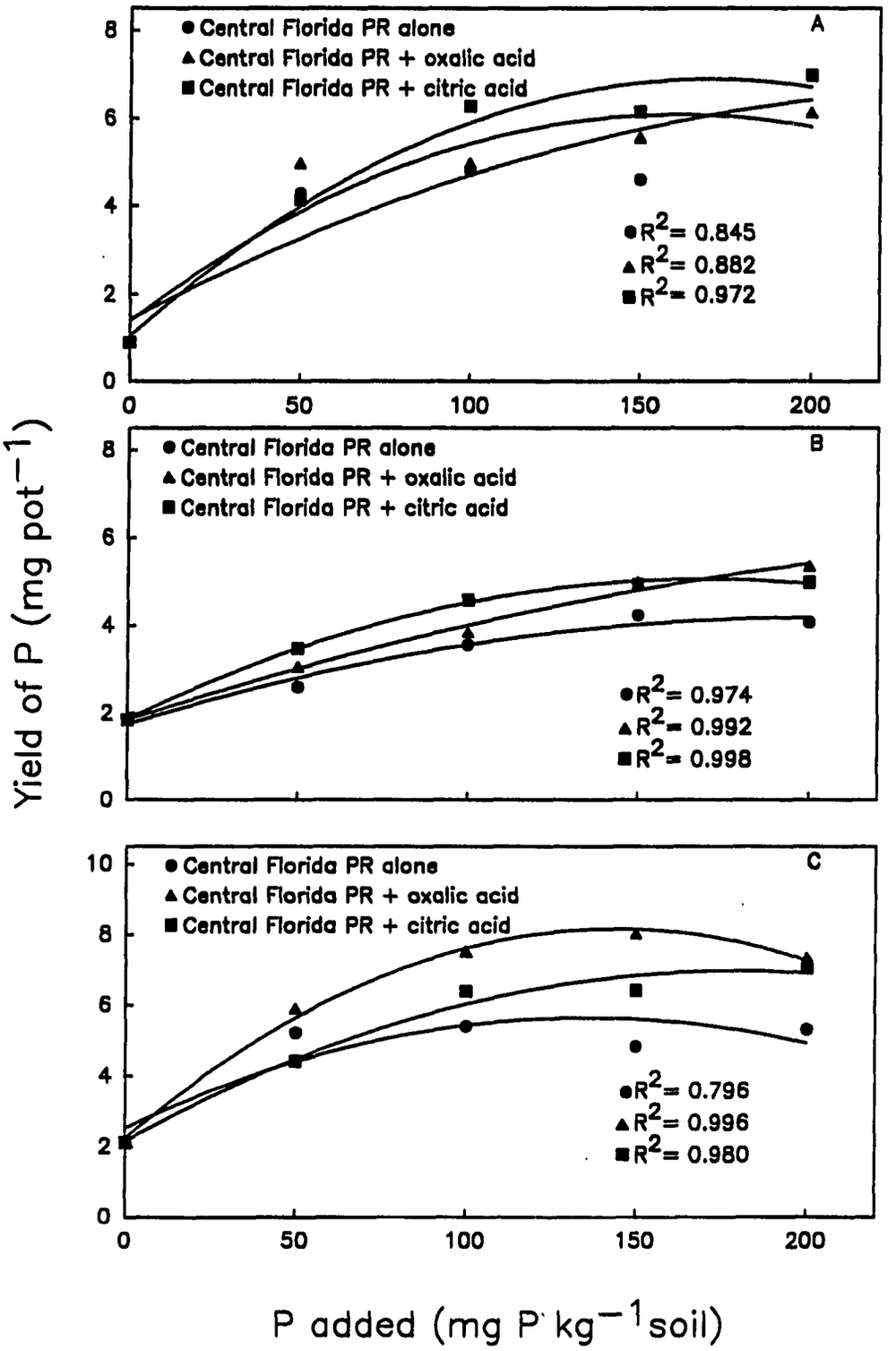

● Central Florida PR alone
▲ Central Florida PR + oxalic acid
■ Central Florida PR + citric acid
A
●R2= 0.845
▲R2= 0.882
■R2= 0.972
B
●R2= 0.974
▲R2= 0.992
■R2= 0.998
C
●R2= 0.796
▲R2= 0.996
■R2= 0.980
Yield of P (mg pot−1)
P added (mg P kg−1soil)

Figure 66. Effect of North Carolina phosphate rock mixed with oxalic or citric acid on P yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

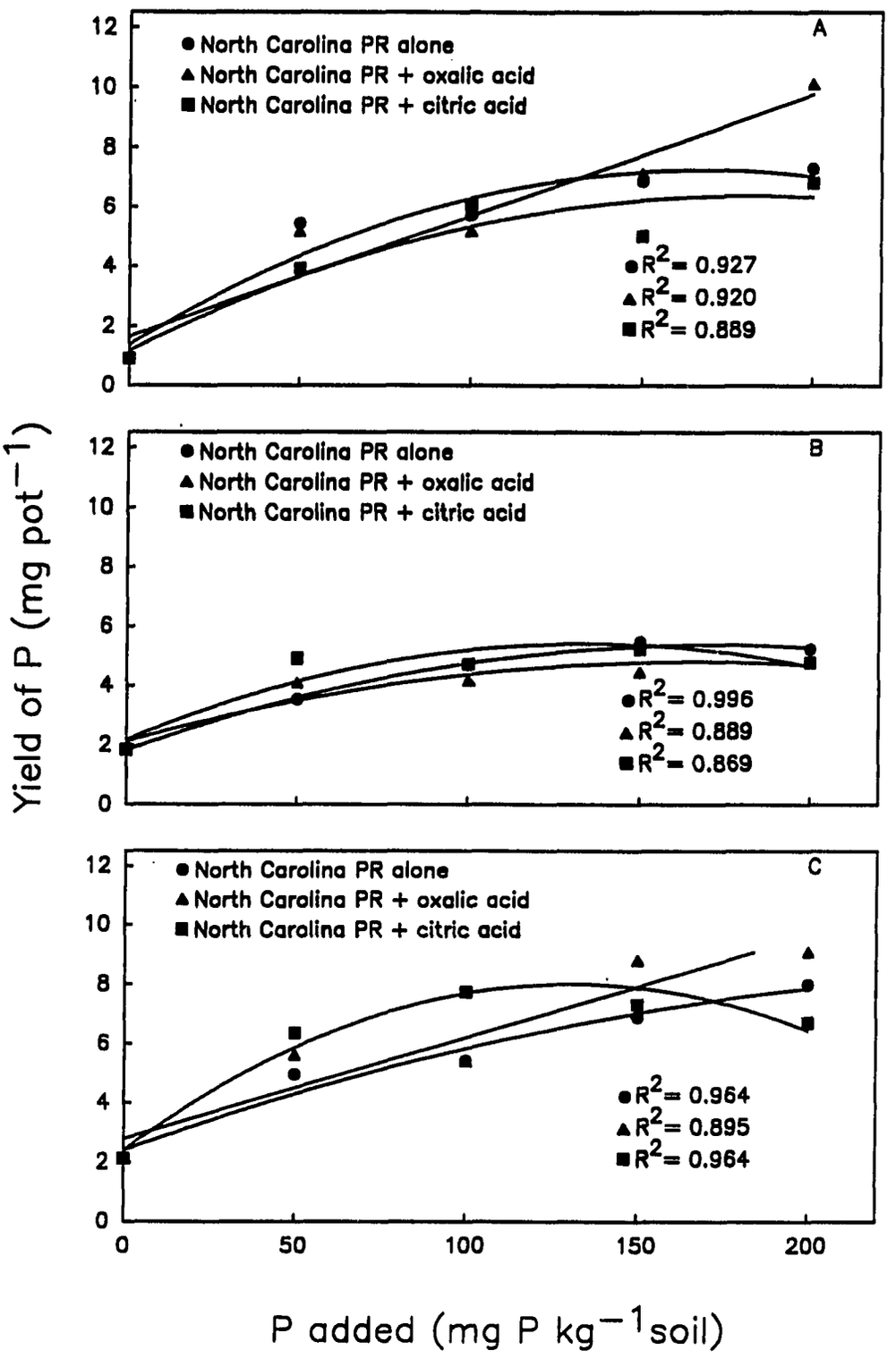

A
● North Carolina PR alone
▲ North Carolina PR + oxalic acid
■ North Carolina PR + citric acid
●R2= 0.927
▲R2= 0.920
■R2= 0.889
B
● North Carolina PR alone
▲ North Carolina PR + oxalic acid
■ North Carolina PR + citric acid
●R2= 0.996
▲R2= 0.889
■R2= 0.869
C
● North Carolina PR alone
▲ North Carolina PR + oxalic acid
■ North Carolina PR + citric acid
●R2= 0.964
▲R2= 0.895
■R2= 0.964
Yield of P (mg pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
10
12
0
50
100
150
200

Figure 67 Effect of Gafsa phosphate rock mixed with oxalic or citric acid on P yield of corn tops produced on Gosport (A), Clinton (B), and Grundy (C) soils under greenhouse conditions

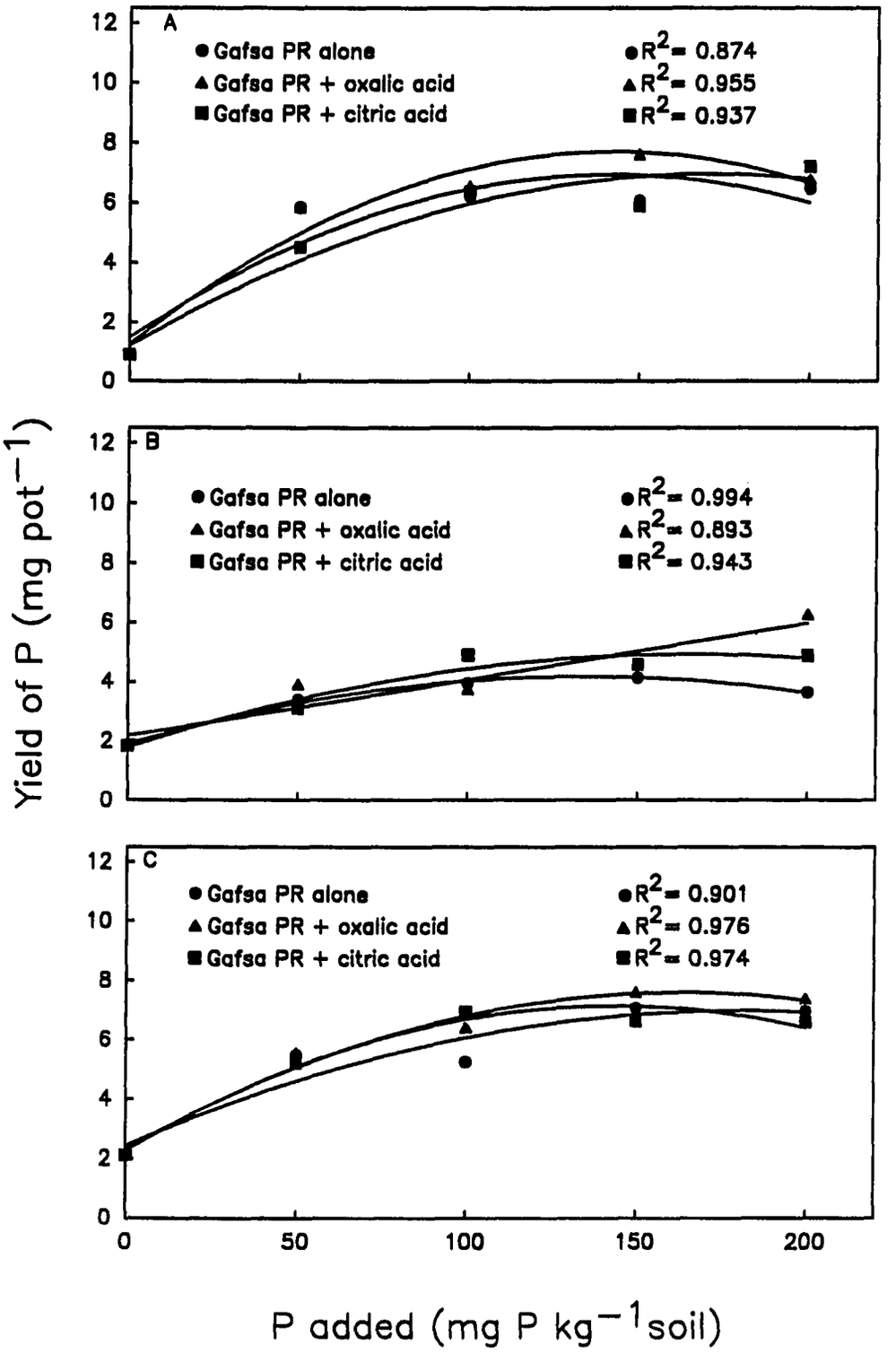

A
● Gafsa PR alone
▲ Gafsa PR + oxalic acid
■ Gafsa PR + citric acid
●R2= 0.874
▲R2= 0.955
■R2= 0.937
B
● Gafsa PR alone
▲ Gafsa PR + oxalic acid
■ Gafsa PR + citric acid
●R2= 0.994
▲R2= 0.893
■R2= 0.943
C
● Gafsa PR alone
▲ Gafsa PR + oxalic acid
■ Gafsa PR + citric acid
●R2= 0.901
▲R2= 0.976
■R2= 0.974
Yield of P (mg pot−1)
P added (mg P kg−1soil)
0
2
4
6
8
10
12
0
50
100
150
200

Figure 68. Relationship between dry matter yield of corn tops and P uptake from Gosport soil treated with four rates of P as Kodjari, North Carolina, Gafsa, Tilemsi valley, Central Florida, or Hahotoe phosphate rock with and without oxalic acid or citric acid treatment

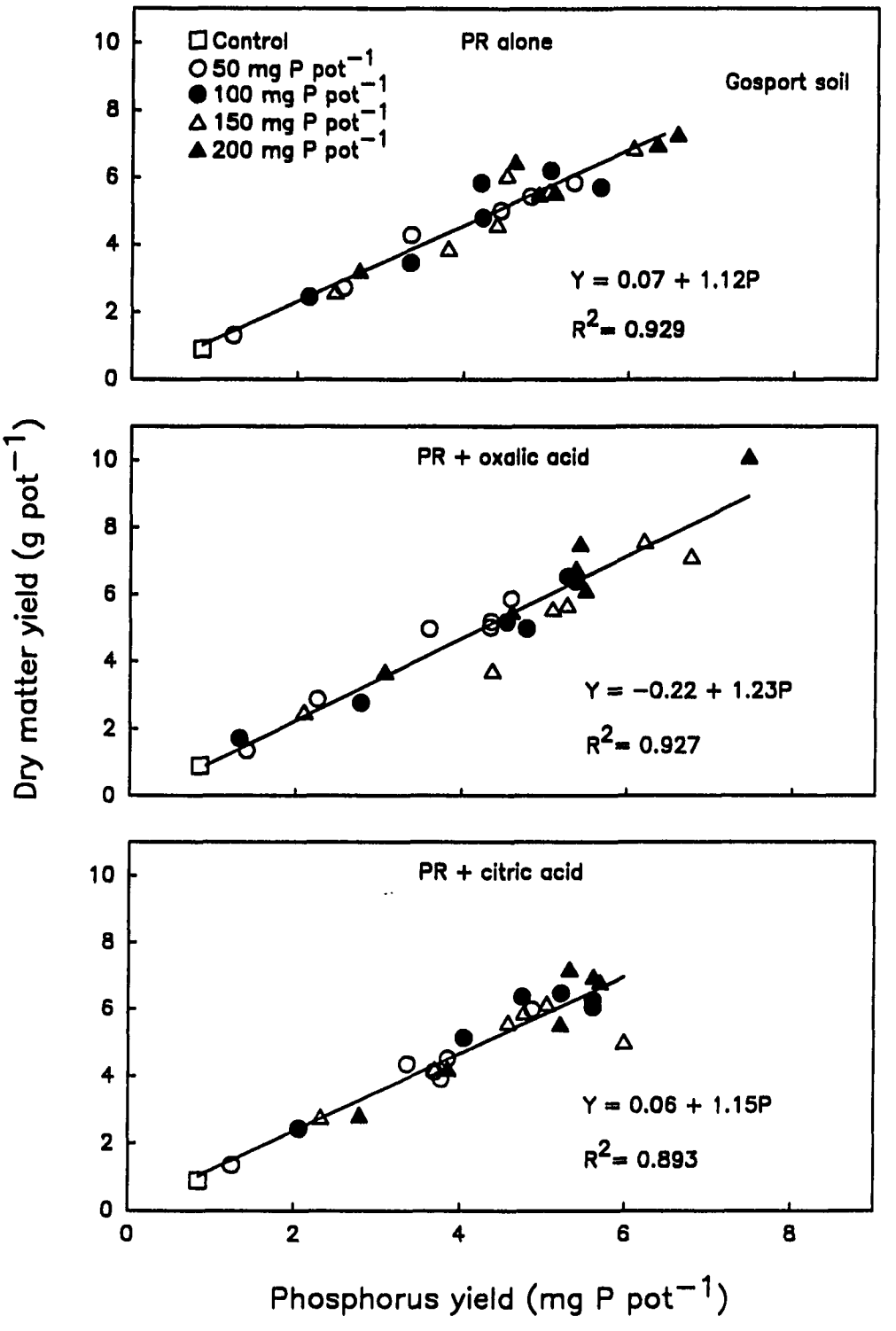

Control
50 mg P pot^{-1}
100 mg P pot^{-1}
150 mg P pot^{-1}
200 mg P pot^{-1}
PR alone
Gosport soil
Y = 0.07 + 1.12P
R^2= 0.929
PR + oxalic acid
Y = −0.22 + 1.23P
R^2= 0.927
PR + citric acid
Y = 0.06 + 1.15P
R^2= 0.893
Dry matter yield (g pot^{-1})
Phosphorus yield (mg P pot^{-1})
0
2
4
6
8
10

Figure 69. Relationship between dry matter yield of corn tops and P uptake from Clinton soil treated with four rates of P as Kodjari, North Carolina, Gafsa, Tilemsi valley, Central Florida, or Hahotoe phosphate rock with and without oxalic acid or citric acid treatment

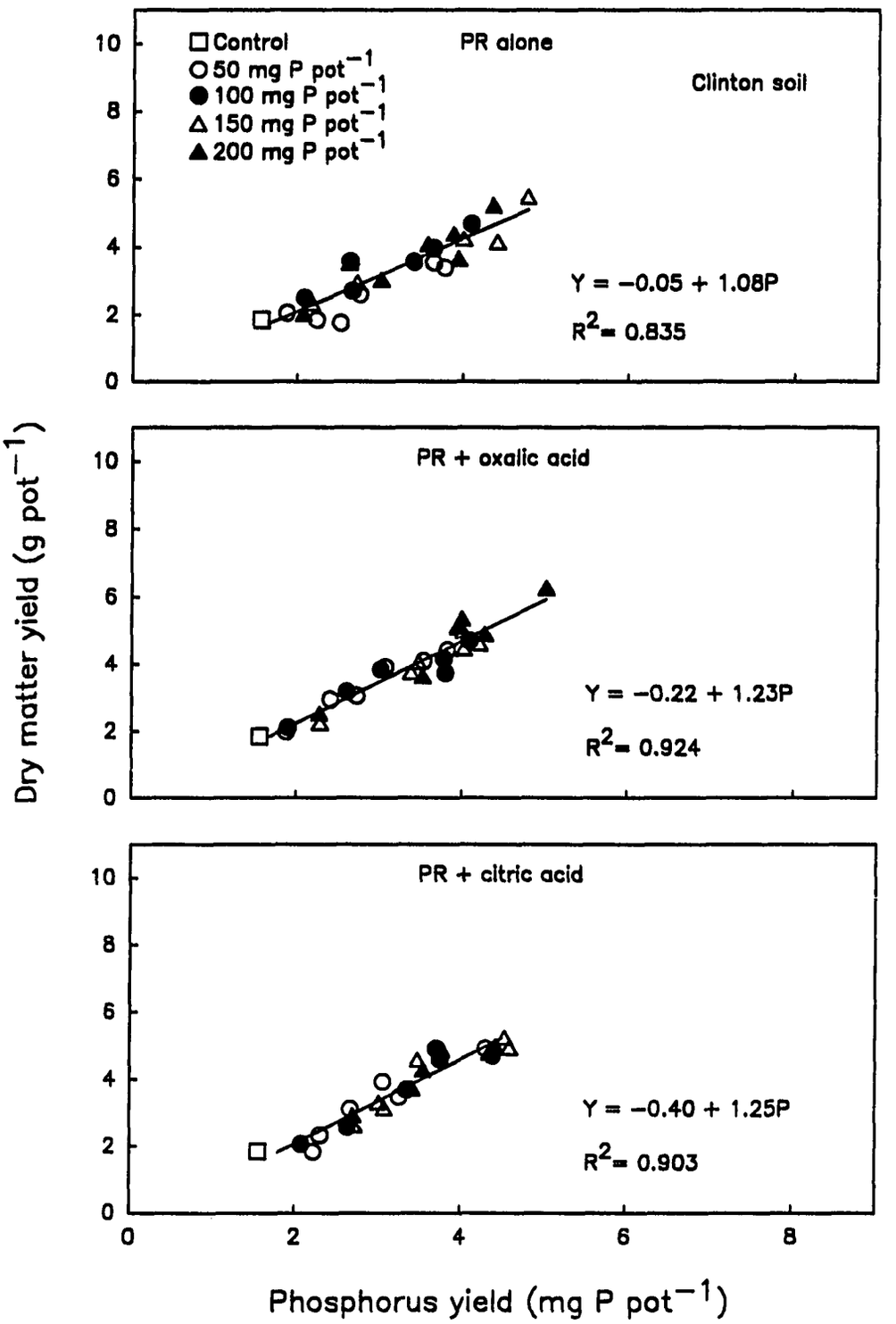
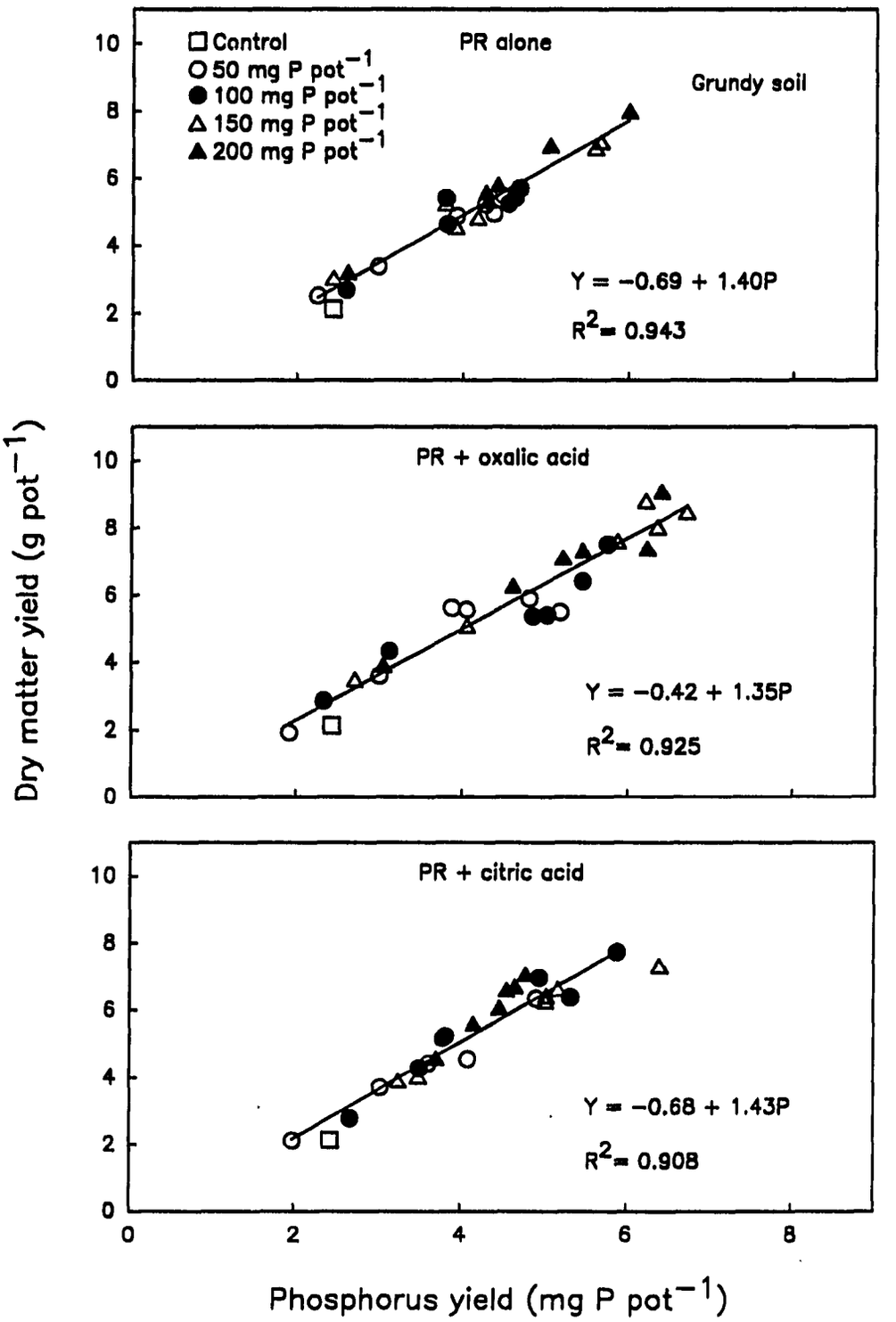

Control
50 mg P pot^{-1}
100 mg P pot^{-1}
150 mg P pot^{-1}
200 mg P pot^{-1}
PR alone
Clinton soil
Y = −0.05 + 1.08P
R^2= 0.835
PR + oxalic acid
Y = −0.22 + 1.23P
R^2= 0.924
PR + citric acid
Y = −0.40 + 1.25P
R^2= 0.903
Dry matter yield (g pot^{-1})
Phosphorus yield (mg P pot^{-1})
0
2
4
6
8
10

Figure 70. Relationship between dry matter yield of corn tops and P uptake from Grundy soil treated with four rates of P as Kodjari, North Carolina, Gafsa, Tilemsi valley, Central Florida, or Hahotoe phosphate rock with and without oxalic acid or citric acid treatment


Control
50 mg P pot^{-1}
100 mg P pot^{-1}
150 mg P pot^{-1}
200 mg P pot^{-1}
PR alone
Grundy soil
Y = −0.69 + 1.40P
R^2= 0.943
PR + oxalic acid
Y = −0.42 + 1.35P
R^2= 0.925
PR + citric acid
Y = −0.68 + 1.43P
R^2= 0.908
Dry matter yield (g pot^{-1})
Phosphorus yield (mg P pot^{-1})
0
2
4
6
8
10

comparison of the internal efficiency of the fertilizer nutrient in all the P fertilizer materials used. The closeness of all the points to the regression lines indicates that the effectiveness of a unit quantity of P taken up by corn in increasing the dry matter yield of this crop did not differ among the P fertilizer materials studied. Because the P fertilizer materials used provided different quantities of P at the same application rate, the data points for the different P fertilizer materials fell at different locations on the regression lines. Similar results were obtained by Khasawneh and Doll (1978) who compared the internal efficiency of P derived from triple superphosphate and six PRs (North Carolina, North Florida, Central Florida, Idaho, Tennessee, and Missouri) in a greenhouse experiment using corn as a test crop.

SUMMARY AND CONCLUSIONS

One of the oldest activities to which human civilization has devoted attention since the appearance of homo sapiens on Earth is agriculture. Before dressing up and philosophizing, man must feed himself. If this statement is true, then the food crisis that is devastating the developing world is a shame not only to the developing countries that could not single out their priorities, but also a shame to the developed World providing the developing World with food assistance instead of giving them the chance to become self-sufficient in food production. Intensive use of agricultural lands in the tropics without return of crop residues has reduced drastically the productivity level of land during the past four decades. Cost of commercial fertilizers which can be used to improve crop yield is skyrocketing, and resource poor farmers in the developing World can no longer afford to buy fertilizers. One of the most limiting nutrients for plant growth under tropical conditions is phosphorus. Almost all the manufactured phosphate fertilizers are produced from phosphate rocks. Countries with indigenous phosphate rock deposits can utilize these raw materials in agriculture and cut down cost on import of water-soluble P fertilizers. The problem related to the use of phosphate rock for direct application is that the rocks do not contain water-soluble P and, therefore, their effectiveness to increase crop yield depends on soil and environmental conditions. Research must, therefore, be focused on relatively inexpensive ways to increase P availability from PRs. Low-molecular-weight organic acids that are exuded from living plant roots into soils or by microbial activities have the ability to complex

polyvalent cations (Al, Fe, and Ca) from PR and release P for plant uptake. The release and phytoavailability of phosphorus in soils treated with phosphate rocks and organic acids warrant special attention. The objectives of this work were: (1) to quantify trace and nontrace metal content of PRs, (2) to evaluate P release from phosphate rocks by several organic and mineral acids, (3) to evaluate the influence of free carbonate content on P release from PRs by selected organic and sulfuric acids, (4) to study the P release from phosphate rocks mixed with organic acid and added to soils under laboratory conditions, and (5) to assess the phytoavailability of phosphorus in soils treated with phosphate rocks and organic acids. The findings can be summarized as follows:

1. The unit-cell a dimension values obtained for the 12 rocks were close to the published values. The unit-cell a dimension and P solubility in neutral ammonium (first extraction) and 2% formic acid were correlated.

2. The studies on trace and nontrace metal content of PRs showed that, besides the elements that appear in the empirical formula of apatite, other elements such as Al and Fe are present in substantial quantities in some PRs. The form in which these elements are found in PR (bound to P or as Al/Fe oxides) played a determinant role in release of P from these rocks by organic acids. In addition to several nontrace metals (Al, Ba, Ca, Fe, K, Mg, Na, and Sr), many trace metals (Cd, Co, Cu, Cr, Li, Mn, Ni, Pb, Rb, and Zn) were found in the 12 rock samples studied. The concentrations of these metals in PRs varied considerably. Cesium was not found in any of the PR

samples. Production, distribution, and transport of PRs would contribute to trace metal enrinchment of soils when PRs are added to soils. Similarly, many trace metals are found in P fertilizers derived from the PRs used in manufacturing the P fertilizers.

3. The release of phosphorus from PR by 1 mM citric acid was affected by the source of the PR and the equilibration time. The amount of P released at any time was not related to the reactivity scale of the PRs.

4. The results suggested that the effectiveness of organic acids to release P from PR is mainly determined by the chemical structure, type and position of the functional group of the ligand and by the relative stability of the metallo-organic complexes formed. The monocarboxylic acids (glycolic, pyruvic, and salicylic) were less effective than the dicarboxylic acids (oxalic, malonic, fumaric, and tartaric), which, in turn, were less effective than the tricarboxylic acid group (cis-aconitic and citric), with the exception of oxalic acid which was equally effective as sulfuric acid.

5. At 1 mM acid, citric and oxalic acids were more effective than sulfuric acid in releasing P from Kodjari and North Florida PRs. Increasing the acid concentration from 1 to 10 mM corresponded to almost a 10-fold increase in P release. At 10 mM acid, the amounts of P released from these two PRs by oxalic and sulfuric acids were the greatest as compared with those released by the other organic and mineral acids studied.

6. In general, aliphatic acids with β-hydroxyl and α-carboxyl groups were more efficient than other aliphatic or aromatic acids in releasing P from PRs.

7. Two successive digestions of phosphate rocks in 0.5 M triammonium citrate solution (pH 8.1 ± 0.1) did not completely remove carbonate of the phosphate rock samples. The digestion of rocks in the triammonium citrate solution positively affected P release from phosphate rocks independently of their reactivity.

8. Analysis of PRs after free carbonate removal showed that more P was released from the low reactive PRs than from the high reactive PRs. Release of Al and Fe was also greater from low reactive than from high reactive PRs. Removal of free carbonate from PRs significantly altered the relationship between P and Ca and Mg. In many cases, the relationship between the amounts of P and Al released without carbonate removal were significantly correlated.

9. The amount of P extracted by the Pi filter paper method from MCP added to soils decreased systematically with increasing incubation time and varied with the soils used.

10. The percentage of plant-availabile P released from PR treated with organic acids and incubated with soils at 25°C under laboratory conditions varied considerably and was related to the reactivity of the rocks. Incubation time of 30 days corresponded to the maximum percentage of P release, and many organic acid treatments were better than PR alone.

11. Greenhouse experiments with corn grown for 60 days on three soils (Gosport, Clinton, and Grundy) treated with one of four rates of P (50, 100, 150, and 200) as PR (Kodjari, North Carolina, Gafsa, Tilemsi Valley, Central Florida, or

Hahotoe) with and without organic acid (oxalic or citric) showed that corn dry matter yield obtained without addition of P was very low and was affected by the soil type. The dry matter and P yields produced on Clinton soil tended to be lower than those produced on Gosport and Grundy soils.

12. In direct application (no organic acid added), as expected, the high reactive PRs were more effective in increasing dry matter and P yields than the medium and the low reactive PRs. In general, the order of dry matter and P yield production was North Carolina PR ≥ Gafsa PR > Tilemsi Valley PR ≥ Central Florida PR > Hahotoe PR ≥ Kodjari PR.

13. Application of monocalcium phosphate increased both dry matter yield and P uptake on all three soils; the increase, however, was not linear.

14. Application of organic acids to soils did not significantly increase the uptake of native P by plants. Corn response to addition of oxalic or citric acid varied with P rates and PR sources. Treatment of Tilemsi Valley and Central Florida PRs with organic acids increased significantly the dry matter yields. These results suggest that organic acids have potential as amendments for increasing plant-available P in PRs added to soils.

15. The relationships between the dry matter yield and yield of P of corn tops produced on Gosport, Clinton, and Grundy soils were significantly correlated ($p < 0.001$). The high correlation coefficients and closeness of all the points to the regression lines indicate that the effectiveness of a unit quantity of P taken up by corn in

increasing the dry matter yield of this crop did not differ among the P fertilizer materials studied. Because the P fertilizer materials used provided different quantities of P at the same application rate, the data points for the different P fertilizer materials fall at different locations on the regression lines.

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APPENDIX

Table 24. Possible structural configurations of aliphatic and aromatic acids used

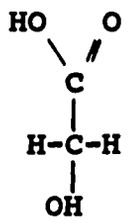
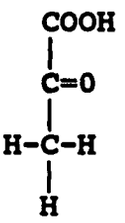
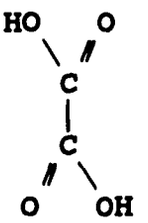
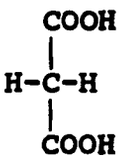
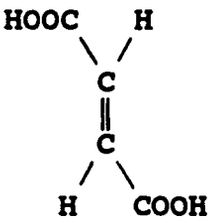
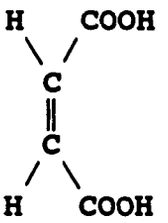
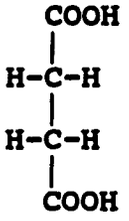
Structural configuration
Aliphatic acids
 Glycolic
 Pyruvic
 Oxalic
 Malonic
 Fumaric
 Maleic

Table 24. Continued

Structural Configuration
Aliphatic acids

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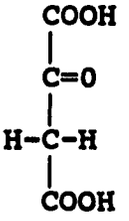
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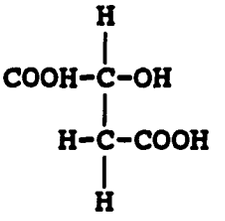
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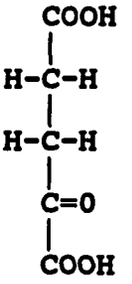
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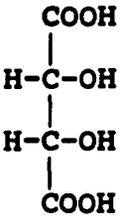
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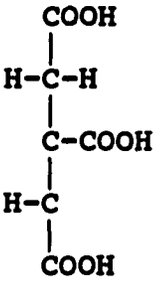
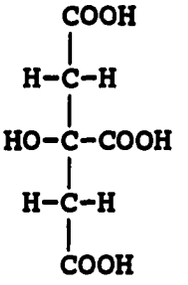
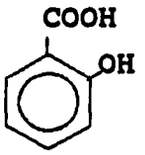

cis-Aconitic

Citric

Table 24. Continued

Structural Configuration
Aromatic acids

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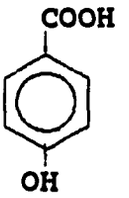
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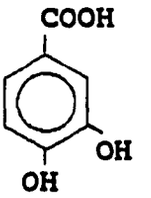
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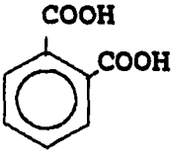
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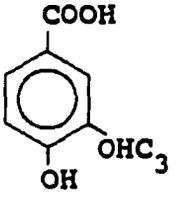
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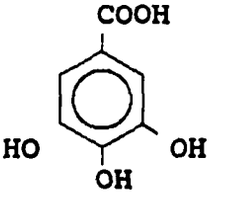
Gallic

Table 25. Amounts of P, Ca, and Mg, released from Kodjari phosphate rock with 1 mM and 10 mM mineral and organic acids

	Metal released with concentration specified					
	1 mM			10 mM		
Acid	P	Ca	Mg	P	Ca	Mg
	mmol kg^{-1}					
Mineral acids						
Hydrochloric	5.38	10.5	0.98	68.7	142	2.91
Nitric	5.92	11.5	0.93	77.4	156	2.68
Sulfuric	11.9	17.5	1.07	156	289	2.95
Aliphatic acids						
Glycolic	4.24	10.0	1.14	30.4	76.1	2.41
Pyruvic	5.38	9.68	0.70	56.8	119	2.68
Oxalic	13.5	7.09	0.92	168	81.4	2.81
Malonic	8.31	15.2	1.16	74.7	134	2.40
Fumaric	7.86	18.5	1.26	52.9	119	2.68
Maleic	5.98	13.9	1.11	67.5	145	2.67
Succinic	4.34	12.5	1.14	20.3	53.1	2.41
Oxalacetic	5.44	11.3	0.91	66.9	131	2.41
Malic	7.65	13.8	1.10	48.4	95.6	3.75
α-Ketoglutaric	7.02	13.3	0.95	68.3	147	2.66
Tartaric	9.27	17.8	1.11	63.6	122	2.64
cis-Aconitic	9.06	14.4	1.12	67.4	140	2.67
Citric	16.4	21.8	1.43	78.9	143	2.81
Aromatic acids						
Salicylic	5.50	11.4	0.91	52.0	110	2.41
p-Hydroxybenzoic	3.35	9.51	0.88	13.7	42.5	1.87
Protocatechuic	3.78	8.95	0.98	12.8	38.9	2.14
Phthalic	6.07	12.2	0.96	50.2	108	2.40
Vanillic	4.30	7.16	0.69	14.9	46.0	2.11
Gallic	4.24	9.31	1.02	17.7	44.2	2.10

Table 26. Amounts of P, Ca, and Mg, released from North Florida phosphate rock with 1 mM and 10 mM mineral and organic acids

Acid	Metal released with concentration specified					
	1 mM			10 mM		
	P	Ca	Mg	P	Ca	Mg
	mmol kg^{-1}					
Mineral acids						
Hydrochloric	0.99	7.72	1.00	53.8	139	11.3
Nitric	1.14	10.8	3.91	63.0	156	12.7
Sulfuric	4.42	19.9	5.17	137	300	15.5
Aliphatic acids						
Glycolic	1.32	10.8	3.80	42.3	121	13.2
Pyruvic	1.38	12.8	4.17	52.0	137	12.4
Oxalic	4.50	5.97	3.65	142	73.5	12.1
Malonic	3.20	14.9	4.84	75.3	158	13.4
Fumaric	2.96	17.8	5.40	74.7	192	14.5
Maleic	2.06	16.7	6.17	61.5	154	12.9
Succinic	1.46	16.2	5.98	34.3	107	13.4
Oxalacetic	1.50	12.4	4.74	58.8	145	12.7
Malic	4.01	15.4	4.71	70.8	159	13.7
α-Ketoglutaric	3.29	14.3	4.99	74.6	180	13.4
Tartaric	5.26	17.9	5.64	98.6	208	14.2
cis-Aconitic	5.95	18.0	5.53	82.1	202	14.5
Citric	13.5	21.6	4.99	113	213	14.5
Aromatic acids						
Salicylic	1.34	12.0	4.29	53.2	140	12.9
p-Hydroxybenzoic	1.20	14.2	5.37	22.4	81.4	11.9
Protocatechuic	1.94	9.18	3.57	24.5	77.9	13.4
Phthalic	3.05	20.2	6.57	61.5	159	13.2
Vanillic	1.05	12.4	4.88	23.3	84.8	12.4
Gallic	3.83	10.8	4.46	32.0	86.5	12.1

Table 27. Amount of Ca, Mg, Al, Fe, and P released from phosphate rocks with 10mM glycolic, pyruvic, oxalic, malonic, or fumaric acids

Acid / Element released	Phosphate rock[a]			
	Kodjari	Tahoua	North Carolina	Gafsa
	mmol kg^{-1}			
Glycolic				
Ca	59.3 (49.9)	84.6 (25.0)	135. (73.5)	169. (65.6)
Mg	1.12 (0.20)	11.3 (0.20)	7.48 (1.60)	15.2 (10.4)
Al	5.53	2.68	0	0
Fe	0.03	0	0	0
P	24.4 (39.1)	20.7 (41.4)	0.16 (28.7)	0. (8.45)
Pyruvic				
Ca	120. (99.2)	116. (83.0)	135. (93.2)	164. (72.9)
Mg	2.04 (0.55)	12.0 (0.55)	7.37 (3.03)	13.1 (23.4)
Al	10.2	3.36	0	0
Fe	0.07	0.08	0	0
P	53.2 (67.3)	40.0 (65.0)	0.53 (30.7)	0. (13.5)
Oxalic				
Ca	72.7 (66.7)	79.4 (73.1)	36.7 (38.7)	51.9 (19.4)
Mg	2.16 (0.46)	11.4 (1.16)	8.17 (3.94)	26.8 (23.0)
Al	20.4	6.47	0	0
Fe	0.20	0.05	0	0
P	146. (154)	146. (152)	14.4 (89.8)	3.40 (82.5)
Malonic				
Ca	134. (119)	155. (121)	211. (127)	230. (113)
Mg	1.97 (0.27)	12.8 (0.81)	10.2 (4.07)	24.6 (33.9)
Al	19.5	11.3	1.08	0.72
Fe	3.36	5.14	1.06	0.10
P	64.7 (65.9)	56.8 (68.4)	10.8 (47.3)	3.00 (28.7)
Fumaric				
Ca	132. (147)	160. (147)	280. (195)	285. (170)
Mg	2.26 (1.08)	12.7 (1.08)	11.9 (5.42)	40.5 (36.9)
Al	10.0	5.38	0.36	0.36
Fe	0.03	0.02	0	0.02
P	47.0 (70.7)	45.9 (76.6)	7.72 (61.6)	0.88 (41.1)

[a]Figures in parentheses are the amounts released after free carbonate removal.

Table 27. Continued

Acid Element released	Phosphate rock			
	Khourigba	Tilemsi Valley	Central Florida	Sechura
	mmol kg^{-1}			
Glycolic				
Ca	113. (63.0)	107. (52.5)	119. (93.2)	128. (86.7)
Mg	8.91 (2.00)	16.1 (0.60	13.0 (1.40)	12.0 (1.40)
Al	0	0	1.17	0
Fe	0	0	0	0
P	0. (38.2)	12.5 (37.7)	39.4 (47.0)	0.06 (33.5)
Pyruvic				
Ca	113. (93.2)	113. (72.9)	140. (117)	133. (81.0)
Mg	8.30 (2.75)	16.6 (1.65)	12.5 (1.65)	11.9 (4.13)
Al	0	0	0.34	0
Fe	0	0	0	0
P	0.01 (43.1)	15.3 (51.5)	49.2 (63.6)	0.24 (38.0)
Oxalic				
Ca	16.8 (60.2)	56.6 (45.2)	80.3 (71.0)	66.1 (47.3)
Mg	7.98 (3.24)	14.3 (1.85)	12.5 (2.78)	13.8 (4.40)
Al	0	0	1.53	0
Fe	0	0	0	0
P	30.2 (117)	94.9 (130)	136. (140)	21.4 (111)
Malonic				
Ca	150. (146)	149. (117)	169. (153)	196. (140)
Mg	10.5 (2.44)	17.8 (2.0)	14.3 (2.17)	15.0 (4.07)
Al	1.43	1.43	10.9	1.08
Fe	0.03	0.09	1.49	0.06
P	6.70 (54.0)	36.5 (60.2)	69.7 (70.1)	13.6 (54.0)
Fumaric				
Ca	221. (181)	227. (164)	220. (189)	269. (193)
Mg	13.4 (3.26)	20.1 (2.17)	14.8 (2.17)	15.8 (4.61)
Al	0.36	0.36	3.23	0.36
Fe	0.02	0	0.03	0
P	9.33 (64.5)	47.8 (80.2)	72.7 (87.8)	15.1 (68.1)

Table 27. Continued

Acid Element released	Phosphate rock			
	Minjingu	North Florida	Hahotoe	Parc W
	mmol kg^{-1}			
Glycolic				
Ca	67.6 (51.2)	115 (127)	100 (65.6)	51.1 (91.9)
Mg	36.6 (14.4)	12.8 (4.39)	5.02 (2.80)	0.51 (0.40)
Al	0	0.84	2.01	4.19
Fe	0	0	0	0.34
P	0 (12.8)	38.5 (41.7)	43.0 (48.1)	19.3 (47.8)
Pyruvic				
Ca	66.0 (46.6)	140. (97.2)	143 (83.0)	103 (111)
Mg	36.4 (19.8)	12.9 (1.65)	5.74 (0.28)	0.92 (0.28)
Al	0	0.50	2.68	7.54
Fe	0	0	0	0.95
P	0 (16.0)	48.1 (59.1)	62.0 (67.3)	43.4 (73.2)
Oxalic				
Ca	11.2 (15.1)	79.4 (62.4)	96.4 (86.0)	87.9 (96.8)
Mg	15.2 (15.07)	11.9 (2.78)	6.00 (1.16)	1.77 (1.16)
Al	0	1.53	5.45	13.6
Fe	0	0.01	0.02	8.18
P	0.76 (85.0)	136 (128)	165 (156)	152 (163)
Malonic				
Ca	96.8 (81.3)	166. (142)	164. (149)	131 (144)
Mg	57.0 (31.7)	12.7 (3.26)	8.75 (3.53)	1.56 (0.54)
Al	0.18	16.5	12.0	10.6
Fe	0	1.23	0.67	16.3
P	0 (31.8)	71.5 (66.7)	72.9 (74.4)	57.6 (73.5)
Fumaric				
Ca	147. (146)	207. (195)	187 (183)	101 (166)
Mg	64.4 (36.3)	14.2 (2.170	6.10 (0.27)	1.43 (0.27)
Al	0.36	2.87	3.76	6.99
Fe	0	0.02	0.02	1.14
P	0 (41.7)	72.4 (82.8)	73.4 (83.3)	36.9 (80.5)

Table 28. Amount of Ca, Mg, Al, Fe, and P released from phosphate rocks with 10mM salicylic, tartaric, cis-aconitic, citric, or sulfuric acids

Acid / Element released	Phosphate rock[a]			
	Kodjari	Tahoua	North Carolina	Gafsa
	mmol kg^{-1}			
Salicylic				
Ca	92.4 (09)	105. (107)	126. (97.2)	163. (81.0)
Mg	2.14 (0.55)	11.9 (0.280	8.08 (3.85)	15.7 (27.2)
Al	10.6	4.03	0	0
Fe	0.40	0.28	0.06	0
P	43.0 (64.80)	36.3 (63.9)	0.06 (31.2)	0. (11.8)
Tartaric				
Ca	131. (148)	152. (146)	80.5 (94.6)	93.8 (58.1)
Mg	2.16 (0.70)	12.2 (1.39)	8.86 (5.56)	29.7 (24.80)
Al	13.6	9.37	0	0
Fe	0.47	0.46	0	0
P	59.9 (82.2)	64.0 (72.9)	24.8 (83.0)	8.29 (73.8)
cis-Aconitic				
Ca	113. (153)	156. (155)	264. (20.2)	270. (190)
Mg	2.42 (0.46)	12.1 (0.91)	10.9 (4.80)	34.8 (32.2)
Al	11.6	6.76	0	0
Fe	0.01	0.01	0.01	0
P	53.3 (82.6)	61.3 (82.3)	27.9 (71.4)	13.8 (59.4)
Citric				
Ca	145. (135)	148. (126)	317. (218)	318. (227)
Mg	2.64 (1.37)	12.6 (1.37)	11.8 (4.80)	35.2 (37.7)
Al	20.9	14.5	1.12	0.96
Fe	4.22	8.77	0	0
P	73.1 (80.1)	71.0 (79.4)	48.4 (98.1)	35.4 (83.0)
Sulfuric				
Ca	308. (176)	308. (228)	256. (188)	259. (139)
Mg	2.66 (0.80)	13.9 (1.20)	11.4 (11.2)	27.0 (29.2)
Al	21.9	12.6	0	0
Fe	0.08	0.04	0	0
P	139. (159)	124. (1974)	29.5 (98.2)	4.26 (80.5)

[a]Figures in parentheses are the amounts released after free carbonate removal.

Table 28. Continued

Acid Element released	Phosphate rock			
	Khourigba	Tilemsi Valley	Central Florida	Sechura
	mmol kg^{-1}			
Salicylic				
Ca	105. (126)	105. (97.0)	124. (138)	124. (105)
Mg	8.40 (2.75)	16.0 (1.38)	13.0 (1.93)	12.2 (3.03)
Al	0	0	0.81	0
Fe	0	0	0.05	0.01
P	0. (43.6)	14.6 (51.5)	46.4 (64.2)	0. (38.3)
Tartaric				
Ca	70.1 (108)	99.5 (168)	132. (191)	135. (187)
Mg	10.4 (3.01)	16.3 (2.32)	14.9 (2.78)	13.7 (5.33)
Al	0	0.34	7.66	0.17
Fe	0	0.01	0.11	0
P	42.2 (116)	92.1 (95.4)	97.9 (102)	36.0 (102)
cis-Aconitic				
Ca	200. (204)	190. (159)	188. (198)	217. (194)
Mg	10.9 (2.74)	18.1 (1.83)	14.6 (2.29)	14.4 (4.80)
Al	0	0	3.70	0
Fe	0	0	0.05	0
P	30.9 (76.8)	63.6 (86.5)	78.2 (94.6)	38.7 (85.9)
Citric				
Ca	190. (190)	183. (161)	209. (178)	276. (206)
Mg	9.90 (2.51)	18.4 (2.29)	14.7 (2.29)	16.0 (4.57)
Al	1.93	3.22	15.4	0.96
Fe	0.10	1.12	3.37	0.26
P	46.4 (101)	74.5 (100)	99.6 (104)	67.0 (112)
Sulfuric				
Ca	235. (171)	273. (178)	322. (263)	274. (228)
Mg	11.2 (3.40)	19.3 (1.80)	15.2 (2.40)	15.8 (4.59)
Al	0	0	2.90	0
Fe	0	0	0.04	0
P	36.7 (126)	97.0 (134)	123. (135)	26.2 (112)

Table 28. Continued

Acid Element released	Phosphate rock			
	Minjingu	North Florida	Hahotoe	Parc W
	mmol kg^{-1}			
Salicylic				
Ca	59.0 (60.8)	124. (128)	129. (119)	81.8 (140)
Mg	37.9 (21.7)	12.5 (2.20)	5.86 (0.55)	1.6 (1.10)
Al	0	1.13	2.26	6.29
Fe	0.01	0.06	0.02	1.80
P	0. (15.5)	46.9 (59.7)	58.0 (66.7)	34.1 (69.0)
Tartaric				
Ca	60.6 (73.1)	158. (110)	176. (174)	110. (151)
Mg	47.8 (27.8)	14.4 (2.55)	6.30 (0.46)	1.47 (0.23)
Al	0.34	7.32	7.32	7.49
Fe	0	0.09	0.07	1.78
P	0.44 (80.8)	94.5 (129)	91.7 (102)	48.9 (83.6)
cis-Aconitic				
Ca	101. (151)	188. (194)	174. (178)	99. (161)
Mg	68.4 (35.2)	14.8 (2.29)	6.82 (0.23)	1.65 (0.23)
Al	0	3.06	4.02	5.96
Fe	0	0	0	0.36
P	0.57 (57.8)	76.1 (93.6)	84.3 (91.7)	46.3 (88.5)
Citric				
Ca	255. (145)	215. (196)	179. (182)	120. (141)
Mg	73.9 (35.6)	14.5 (2.51)	6.05 (0.69)	1.54 (0.23)
Al	0.32	21.2	11.6	10.9
Fe	0.31	3.28	0.96	19.2
P	5.68 (89.4)	108. (103)	92.5 (94.6)	70.3 (79.7)
Sulfuric				
Ca	105. (125)	318. (211)	338. (345)	283. (150)
Mg	53.1 (23.0)	13.9 (4.79)	5.84 (0.60)	1.48 (0.40)
Al	0	3.23	8.23	12.3
Fe	0	0.01	0.02	1.27
P	0. (72.4)	121. (140)	152. (116)	126. (119)

Table 29. Phosphorus released at different incubation times (days) in soils treated with Kodjari PR and various organic acids (means of duplicates)

Soil	Organic acid	Incubation time (days) 0	15	30	45
		mg P kg^{-1} soil			
Gosport					
No PR added (control)					
	None	4.70	3.60	4.30	3.82
	Oxalic	4.78	4.02	3.80	3.66
	Tartaric	3.81	3.52	4.10	3.32
	Cis-aconitic	4.30	3.60	3.73	4.32
	Citric	3.85	4.06	3.64	3.71
PR added					
	None	11.0	9.08	7.86	8.26
	Oxalic	10.2	9.08	8.02	9.00
	Tartaric	10.4	7.61	6.04	8.92
	Cis-aconitic	10.6	7.72	7.01	9.00
	Citric	11.0	8.69	7.05	9.18
Clinton					
No PR added (control)					
	None	5.07	4.60	4.26	5.94
	Oxalic	5.48	4.79	4.50	4.17
	Tartaric	5.59	4.91	4.42	4.13
	Cis-aconitic	5.44	4.71	4.62	4.17
	Citric	5.43	4.40	4.70	4.13
PR added					
	None	10.7	12.3	8.63	7.84
	Oxalic	10.5	8.19	8.10	9.04
	Tartaric	10.3	10.2	7.18	6.72
	Cis-aconitic	11.4	7.88	7.06	8.10
	Citric	12.2	9.16	7.62	7.80
Grundy					
No PR added (control)					
	None	4.62	3.75	2.96	2.97
	Oxalic	4.26	3.02	2.68	2.94
	Tartaric	4.06	3.06	2.84	2.70
	Cis-aconitic	3.77	2.74	2.35	1.89
	Citric	3.48	4.10	2.68	3.20
PR added					
	None	9.59	9.87	7.01	7.30
	Oxalic	8.27	10.1	7.58	7.45
	Tartaric	8.80	8.66	6.77	8.76
	Cis-aconitic	8.96	9.52	7.58	8.26
	Citric	10.8	10.7	8.44	7.52

Table 30. Phosphorus released at different incubation times (days) in soils treated with North Carolina PR and various organic acids (means of duplicates)

Soil	Organic acid	Incubation time (days) 0	15	30	45
		----------mg P kg^{-1} soil----------			
Gosport					
No PR added (control)					
	None	4.70	3.60	4.30	3.82
	Oxalic	4.78	4.02	3.80	3.66
	Tartaric	3.81	3.52	4.10	3.32
	Cis-aconitic	4.30	3.60	3.73	4.32
	Citric	3.85	4.06	3.64	3.71
PR added					
	None	98.9	112	116	102
	Oxalic	97.6	108	108	110
	Tartaric	98.7	121	97.0	110
	Cis-aconitic	84.2	103	106	125
	Citric	101	91.7	90.0	98.4
Clinton					
No PR added (control)					
	None	5.07	4.60	4.26	5.94
	Oxalic	5.48	4.79	4.50	4.17
	Tartaric	5.59	4.91	4.42	4.13
	Cis-aconitic	5.44	4.71	4.62	4.17
	Citric	5.43	4.40	4.70	4.13
PR added					
	None	57.4	77.4	42.8	58.8
	Oxalic	52.6	62.9	73.2	71.4
	Tartaric	57.9	65.0	71.9	59.1
	Cis-aconitic	60.1	84.9	68.7	67.2
	Citric	50.9	36.2	73.2	33.6
Grundy					
No PR added (control)					
	None	4.62	3.75	2.96	2.97
	Oxalic	4.26	3.02	2.68	2.94
	Tartaric	4.06	3.06	2.84	2.70
	Cis-aconitic	3.77	2.74	2.35	1.89
	Citric	3.48	4.10	2.68	3.20
PR added					
	None	55.4	99.1	79.2	61.4
	Oxalic	84.8	106	82.4	68.8
	Tartaric	75.8	95.8	94.4	71.0
	Cis-aconitic	76.0	67.7	71.3	67.4
	Citric	80.9	100	102	84.6

Table 31. Phosphorus released at different incubation times (days) in soils treated with Gafsa PR and various organic acids (means of duplicates)

Soil	Organic acid	Incubation time (days) 0	15	30	45
		----------mg P kg^{-1} soil----------			
Gosport					
	No PR added (control)				
	None	4.70	3.60	4.30	3.82
	Oxalic	4.78	4.02	3.80	3.66
	Tartaric	3.81	3.52	4.10	3.32
	Cis-aconitic	4.30	3.60	3.73	4.32
	Citric	3.85	4.06	3.64	3.71
	PR added				
	None	92.2	114	110	110
	Oxalic	83.0	71.0	118	110
	Tartaric	84.0	75.8	114	104
	Cis-aconitic	87.4	75.1	116	104
	Citric	82.5	87.6	124	103
Clinton					
	No PR added (control)				
	None	5.07	4.60	4.26	5.94
	Oxalic	5.48	4.79	4.50	4.17
	Tartaric	5.59	4.91	4.42	4.13
	Cis-aconitic	5.44	4.71	4.62	4.17
	Citric	5.43	4.40	4.70	4.13
	PR added				
	None	42.7	53.8	40.7	46.8
	Oxalic	38.8	41.9	67.5	47.4
	Tartaric	43.6	33.0	71.4	33.8
	Cis-aconitic	39.8	59.4	68.3	58.6
	Citric	41.6	55.2	72.2	54.6
Grundy					
	No PR added (control)				
	None	4.62	3.75	2.96	2.97
	Oxalic	4.26	3.02	2.68	2.94
	Tartaric	4.06	3.06	2.84	2.70
	Cis-aconitic	3.77	2.74	2.35	1.89
	Citric	3.48	4.10	2.68	3.20
	PR added				
	None	76.3	108	81.4	71.4
	Oxalic	66.3	56.7	103	74.3
	Tartaric	62.8	53.6	105	57.5
	Cis-aconitic	71.2	58.9	107	73.4
	Citric	78.2	63.3	98.0	72.2

Table 32. Phosphorus released at different incubation times (days) in soils treated with Tilemsi Valley PR and various organic acids (means of duplicates)

Soil	Organic acid	Incubation time (days) 0	15	30	45
		----------mg P kg^{-1} soil----------			
Gosport					
	No PR added (control)				
	None	4.70	3.60	4.30	3.82
	Oxalic	4.78	4.02	3.80	3.66
	Tartaric	3.81	3.52	4.10	3.32
	Cis-aconitic	4.30	3.60	3.73	4.32
	Citric	3.85	4.06	3.64	3.71
	PR added				
	None	52.2	59.6	53.6	61.2
	Oxalic	48.0	40.0	62.0	51.2
	Tartaric	46.0	32.4	75.0	43.8
	Cis-aconitic	50.2	35.3	64.8	38.2
	Citric	48.2	25.7	67.8	44.6
Clinton					
	No PR added (control)				
	None	5.07	4.60	4.26	5.94
	Oxalic	5.48	4.79	4.50	4.17
	Tartaric	5.59	4.91	4.42	4.13
	Cis-aconitic	5.44	4.71	4.62	4.17
	Citric	5.43	4.40	4.70	4.13
	PR added				
	None	25.2	21.0	19.2	22.4
	Oxalic	22.6	24.2	34.4	21.2
	Tartaric	19.6	14.5	36.4	15.0
	Cis-aconitic	23.8	30.0	33.9	14.8
	Citric	20.4	20.7	28.6	16.3
Grundy					
	No PR added (control)				
	None	4.62	3.75	2.96	2.97
	Oxalic	4.26	3.02	2.68	2.94
	Tartaric	4.06	3.06	2.84	2.70
	Cis-aconitic	3.77	2.74	2.35	1.89
	Citric	3.48	4.10	2.68	3.20
	PR added				
	None	31.8	53.8	38.0	35.0
	Oxalic	41.2	32.4	57.0	43.2
	Tartaric	37.0	21.9	58.4	41.4
	Cis-aconitic	36.4	31.1	59.6	41.8
	Citric	27.8	27.8	54.0	36.0

Table 33. Phosphorus released at different incubation times (days) in soils treated with Central Florida PR and various organic acids (means of duplicates)

Soil	Organic acid	Incubation time (days) 0	15	30	45
		----------mg P kg^{-1} soil----------			
Gosport					
No PR added (control)					
	None	4.70	3.60	4.30	3.82
	Oxalic	4.78	4.02	3.80	3.66
	Tartaric	3.81	3.52	4.10	3.32
	Cis-aconitic	4.30	3.60	3.73	4.32
	Citric	3.85	4.06	3.64	3.71
PR added					
	None	64.6	68.5	54.7	65.5
	Oxalic	61.0	53.4	74.6	70.8
	Tartaric	63.9	38.6	75.8	68.5
	Cis-aconitic	63.9	46.1	75.0	68.3
	Citric	61.4	44.6	74.0	69.3
Clinton					
No PR added (control)					
	None	5.07	4.60	4.26	5.94
	Oxalic	5.48	4.79	4.50	4.17
	Tartaric	5.59	4.91	4.42	4.13
	Cis-aconitic	5.44	4.71	4.62	4.17
	Citric	5.43	4.40	4.70	4.13
PR added					
	None	27.1	30.6	27.5	34.4
	Oxalic	28.2	32.3	44.2	38.6
	Tartaric	28.2	36.1	47.6	35.6
	Cis-aconitic	29.8	29.8	42.2	18.5
	Citric	32.4	16.1	46.2	24.7
Grundy					
No PR added (control)					
	None	4.62	3.75	2.96	2.97
	Oxalic	4.26	3.02	2.68	2.94
	Tartaric	4.06	3.06	2.84	2.70
	Cis-aconitic	3.77	2.74	2.35	1.89
	Citric	3.48	4.10	2.68	3.20
PR added					
	None	38.2	45.4	54.7	48.4
	Oxalic	41.4	30.8	74.4	40.6
	Tartaric	38.6	32.6	72.4	48.8
	Cis-aconitic	39.6	27.2	67.7	44.6
	Citric	37.2	39.5	60.0	52.6

Table 34. Phosphorus released at different incubation times (days) in soils treated with Hahotoe PR and various organic acids (means of duplicates)

Soil	Organic acid	Incubation time (days) 0	15	30	45
		----------mg P kg^{-1} soil----------			
Gosport					
No PR added (control)					
	None	4.70	3.60	4.30	3.82
	Oxalic	4.78	4.02	3.80	3.66
	Tartaric	3.81	3.52	4.10	3.32
	Cis-aconitic	4.30	3.60	3.73	4.32
	Citric	3.85	4.06	3.64	3.71
PR added					
	None	23.2	20.4	20.1	22.5
	Oxalic	22.8	14.7	25.0	17.4
	Tartaric	19.2	15.6	24.0	19.1
	Cis-aconitic	20.8	15.3	26.8	14.6
	Citric	20.7	13.2	24.6	15.2
Clinton					
No PR added (control)					
	None	5.07	4.60	4.26	5.94
	Oxalic	5.48	4.79	4.50	4.17
	Tartaric	5.59	4.91	4.42	4.13
	Cis-aconitic	5.44	4.71	4.62	4.17
	Citric	5.43	4.40	4.70	4.13
PR added					
	None	16.8	18.8	14.8	14.2
	Oxalic	17.6	18.6	18.5	11.0
	Tartaric	12.6	8.96	17.1	15.8
	Cis-aconitic	16.7	11.9	15.2	14.6
	Citric	18.6	15.0	17.7	15.2
Grundy					
No PR added (control)					
	None	4.62	3.75	2.96	2.97
	Oxalic	4.26	3.02	2.68	2.94
	Tartaric	4.06	3.06	2.84	2.70
	Cis-aconitic	3.77	2.74	2.35	1.89
	Citric	3.48	4.10	2.68	3.20
PR added					
	None	20.6	25.6	17.6	19.6
	Oxalic	18.6	16.8	22.4	24.7
	Tartaric	16.0	18.4	21.7	14.4
	Cis-aconitic	18.0	15.4	27.8	16.4
	Citric	19.4	12.9	22.8	15.6

Table 35. Dry matter yield, total P, and P yield of corn tops produced under greenhouse conditions on Gosport soil

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G1	None	Control	0.80	0.114	0.91
G2	None	Control	0.96	0.108	1.03
G3	None	Control	0.80	0.100	0.80
G4	None	Glass beads	0.71	0.114	0.81
G5	None	Glass beads	1.05	0.080	0.84
G6	None	Glass beads	0.71	0.103	0.73
G7	None	Glass beads	0.76	0.093	0.71
G8	None	Glass beads	0.76	0.105	0.80
G9	None	Glass beads	0.69	0.101	0.70
G10	None	Glass beads	0.69	0.087	0.60
G11	None	Glass beads	0.81	0.086	0.70
G12	None	Glass beads	0.74	0.110	0.81
G13	None	Glass beads	0.74	0.101	0.75
G14	None	Glass beads	0.67	0.096	0.64
G15	None	Glass beads	0.87	0.104	0.91
G88	None	Oxalic acid	0.72	0.098	0.70
G89	None	Oxalic acid	0.75	0.112	0.84
G90	None	Oxalic acid	0.91	0.090	0.82
G91	None	Oxalic acid	1.00	0.091	0.87
G92	None	Oxalic acid	1.07	0.086	0.92
G93	None	Oxalic acid	1.07	0.082	0.88
G94	None	Oxalic acid	1.04	0.094	0.98
G95	None	Oxalic acid	0.87	0.105	0.91
G96	None	Oxalic acid	1.20	0.086	1.03

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G97	None	Oxalic acid	1.00	0.082	0.82
G98	None	Oxalic acid	0.89	0.095	0.84
G99	None	Oxalic acid	0.76	0.114	0.86
G100	None	Citric acid	1.20	0.065	0.78
G101	None	Citric acid	1.00	0.073	0.73
G102	None	Citric acid	0.88	0.103	0.91
G103	None	Citric acid	1.03	0.069	0.71
G104	None	Citric acid	0.87	0.103	0.90
G105	None	Citric acid	0.99	0.071	0.70
G106	None	Citric acid	0.65	0.107	0.69
G107	None	Citric acid	0.71	0.082	0.58
G108	None	Citric acid	0.79	0.092	0.73
G109	None	Citric acid	0.78	0.089	0.69
G110	None	Citric acid	0.61	0.105	0.64
G111	None	Citric acid	1.04	0.093	0.97
G16	Kodjari	50	1.26	0.124	1.56
G17	Kodjari	50	1.31	0.098	1.28
G18	Kodjari	50	1.10	0.100	1.10
G19	Kodjari	100	1.99	0.131	2.60
G20	Kodjari	100	2.05	0.108	2.20
G21	Kodjari	100	2.34	0.108	2.52
G22	Kodjari	150	2.11	0.109	2.31
G23	Kodjari	150	2.67	0.101	2.69
G24	Kodjari	150	2.56	0.109	2.80

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G25	Kodjari	200	2.97	0.133	3.94
G26	Kodjari	200	2.99	0.100	3.00
G27	Kodjari	200	2.27	0.119	2.69
G28	N. Carolina	50	4.73	0.106	5.01
G29	N. Carolina	50	5.42	0.122	6.61
G30	N. Carolina	50	4.29	0.109	4.69
G31	N. Carolina	100	5.87	0.111	6.51
G32	N. Carolina	100	4.67	0.111	5.16
G33	N. Carolina	100	6.43	0.085	5.45
G34	N. Carolina	150	5.82	0.121	7.03
G35	N. Carolina	150	6.31	0.115	7.25
G36	N. Carolina	150	6.04	0.105	6.33
G37	N. Carolina	200	7.19	0.105	7.54
G38	N. Carolina	200	6.01	0.106	6.39
G39	N. Carolina	200	6.55	0.121	7.93
G40	Gafsa	50	5.62	0.098	5.50
G41	Gafsa	50	5.19	0.112	5.84
G42	Gafsa	50	5.20	0.119	6.20
G43	Gafsa	100	5.28	0.122	6.45
G44	Gafsa	100	5.47	0.125	6.83
G45	Gafsa	100	4.41	0.120	5.31
G46	Gafsa	150	4.56	0.149	6.78
G47	Gafsa	150	4.42	0.122	5.40
G48	Gafsa	150	4.57	0.131	6.00

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G49	Gafsa	200	4.46	0.126	5.64
G50	Gafsa	200	4.62	0.146	6.74
G51	Gafsa	200	4.95	0.141	7.00
G52	Tilemsi	50	4.58	0.090	4.11
G53	Tilemsi	50	4.43	0.121	5.37
G54	Tilemsi	50	4.30	0.129	5.56
G55	Tilemsi	100	4.20	0.126	5.29
G56	Tilemsi	100	4.45	0.131	5.82
G57	Tilemsi	100	3.95	0.163	6.42
G58	Tilemsi	150	4.72	0.127	6.01
G59	Tilemsi	150	5.43	0.097	5.28
G60	Tilemsi	150	4.95	0.111	5.48
G61	Tilemsi	200	5.15	0.105	5.40
G62	Tilemsi	200	4.29	0.122	5.22
G63	Tilemsi	200	5.28	0.111	5.87
G64	C. Florida	50	3.92	0.115	4.49
G65	C. Florida	50	2.99	0.142	4.25
G66	C. Florida	50	3.16	0.130	4.09
G67	C. Florida	100	4.65	0.096	4.45
G68	C. Florida	100	4.09	0.133	5.42
G69	C. Florida	100	3.91	0.116	4.52
G70	C. Florida	150	4.81	0.099	4.75
G71	C. Florida	150	4.49	0.118	5.30
G72	C. Florida	150	3.90	0.142	5.55

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G73	C. Florida	200	6.34	0.116	7.35
G74	C. Florida	200	6.27	0.116	7.30
G75	C. Florida	200	6.40	0.098	6.28
G76	Hahotoe	50	2.71	0.076	2.07
G77	Hahotoe	50	2.28	0.131	2.99
G78	Hahotoe	50	2.65	0.116	3.09
G79	Hahotoe	100	2.95	0.105	3.10
G80	Hahotoe	100	3.52	0.116	4.07
G81	Hahotoe	100	3.57	0.089	3.19
G82	Hahotoe	150	3.40	0.093	3.17
G83	Hahotoe	150	3.86	0.118	4.54
G84	Hahotoe	150	4.17	0.094	3.90
G85	Hahotoe	200	5.20	0.112	5.82
G86	Hahotoe	200	4.94	0.118	5.83
G87	Hahotoe	200	5.19	0.097	5.02
G112	Kodjari	50 + Oxal	1.44	0.117	1.69
G113	Kodjari	50 + Oxal	1.29	0.086	1.11
G114	Kodjari	50 + Oxal	1.50	0.085	1.27
G115	Kodjari	100 + Oxal	1.48	0.106	1.57
G116	Kodjari	100 + Oxal	1.32	0.149	1.97
G117	Kodjari	100 + Oxal	1.16	0.155	1.80
G118	Kodjari	150 + Oxal	1.95	0.111	2.17
G119	Kodjari	150 + Oxal	2.24	0.132	2.96
G120	Kodjari	150 + Oxal	2.10	0.094	2.35

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G121	Kodjari	200 + Oxal	3.06	0.131	4.00
G122	Kodjari	200 + Oxal	3.19	0.108	3.45
G123	Kodjari	200 + Oxal	2.95	0.123	3.61
G124	N. Carolina	50 + Oxal	4.99	0.115	5.72
G125	N. Carolina	50 + Oxal	3.95	0.128	5.06
G126	N. Carolina	50 + Oxal	4.11	0.116	4.76
G127	N. Carolina	100 + Oxal	3.72	0.139	5.18
G128	N. Carolina	100 + Oxal	5.39	0.126	6.82
G129	N. Carolina	100 + Oxal	4.51	0.120	5.42
G130	N. Carolina	150 + Oxal	6.31	0.119	7.50
G131	N. Carolina	150 + Oxal	7.01	0.108	7.59
G132	N. Carolina	150 + Oxal	7.00	0.090	6.30
G133	N. Carolina	200 + Oxal	7.40	0.147	10.88
G134	N. Carolina	200 + Oxal	7.58	0.132	10.02
G135	N. Carolina	200 + Oxal	7.41	0.127	9.44
G136	Gafsa	50 + Oxal	4.60	0.130	5.99
G137	Gafsa	50 + Oxal	4.12	0.131	5.41
G138	Gafsa	50 + Oxal	5.09	0.122	6.19
G139	Gafsa	100 + Oxal	5.31	0.130	6.91
G140	Gafsa	100 + Oxal	5.28	0.120	6.34
G141	Gafsa	100 + Oxal	5.26	0.120	6.33
G142	Gafsa	150 + Oxal	6.27	0.128	8.02
G143	Gafsa	150 + Oxal	5.70	0.136	7.75
G144	Gafsa	150 + Oxal	6.66	0.105	7.03

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G145	Gafsa	200 + Oxal	4.88	0.127	6.22
G146	Gafsa	200 + Oxal	5.38	0.121	6.51
G147	Gafsa	200 + Oxal	5.88	0.129	7.59
G148	Tilemsi	50 + Oxal	4.21	0.131	5.50
G149	Tilemsi	50 + Oxal	4.80	0.089	4.28
G150	Tilemsi	50 + Oxal	4.00	0.131	5.24
G151	Tilemsi	100 + Oxal	5.70	0.116	6.64
G152	Tilemsi	100 + Oxal	5.07	0.121	6.15
G153	Tilemsi	100 + Oxal	5.37	0.118	6.35
G154	Tilemsi	150 + Oxal	5.14	0.088	4.52
G155	Tilemsi	150 + Oxal	5.43	0.125	6.80
G156	Tilemsi	150 + Oxal	5.28	0.108	5.71
G157	Tilemsi	200 + Oxal	5.49	0.146	7.99
G158	Tilemsi	200 + Oxal	5.43	0.140	7.60
G159	Tilemsi	200 + Oxal	5.37	0.130	6.97
G160	C. Florida	50 + Oxal	3.48	0.117	4.07
G161	C. Florida	50 + Oxal	3.73	0.156	5.83
G162	C. Florida	50 + Oxal	3.60	0.139	5.01
G163	C. Florida	100 + Oxal	4.39	0.094	4.11
G164	C. Florida	100 + Oxal	4.77	0.122	5.82
G165	C. Florida	100 + Oxal	5.19	0.096	4.97
G166	C. Florida	150 + Oxal	5.23	0.092	4.83
G167	C. Florida	150 + Oxal	5.35	0.113	6.05
G168	C. Florida	150 + Oxal	4.76	0.122	5.80

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G169	C. Florida	200 + Oxal	5.68	0.123	7.01
G170	C. Florida	200 + Oxal	5.46	0.099	5.43
G171	C. Florida	200 + Oxal	5.36	0.111	5.96
G172	Hahotoe	50 + Oxal	2.15	0.119	2.56
G173	Hahotoe	50 + Oxal	2.50	0.132	3.29
G174	Hahotoe	50 + Oxal	2.13	0.130	2.78
G175	Hahotoe	100 + Oxal	2.78	0.092	2.57
G176	Hahotoe	100 + Oxal	2.63	0.086	2.25
G177	Hahotoe	100 + Oxal	2.94	0.119	3.51
G178	Hahotoe	150 + Oxal	4.64	0.079	3.65
G179	Hahotoe	150 + Oxal	3.93	0.079	2.10
G180	Hahotoe	150 + Oxal	4.54	0.098	4.46
G181	Hahotoe	200 + Oxal	4.51	0.112	5.07
G182	Hahotoe	200 + Oxal	4.58	0.120	5.51
G183	Hahotoe	200 + Oxal	4.75	0.123	5.82
G184	Kodjari	50 + Citr	1.11	0.117	1.30
G185	Kodjari	50 + Citr	1.25	0.102	1.28
G186	Kodjari	50 + Citr	1.39	0.105	1.46
G187	Kodjari	100 + Citr	2.30	0.123	2.84
G188	Kodjari	100 + Citr	2.17	0.102	2.22
G189	Kodjari	100 + Citr	1.70	0.133	2.26
G190	Kodjari	150 + Citr	2.14	0.122	2.62
G191	Kodjari	150 + Citr	2.69	0.110	2.97
G192	Kodjari	150 + Citr	2.13	0.130	2.76

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G193	Kodjari	200 + Citr	2.42	0.111	2.69
G194	Kodjari	200 + Citr	2.86	0.099	2.83
G195	Kodjari	200 + Citr	3.10	0.097	3.01
G196	N. Carolina	50 + Citr	4.09	0.104	4.25
G197	N. Carolina	50 + Citr	3.41	0.109	3.70
G198	N. Carolina	50 + Citr	3.81	0.099	3.79
G199	N. Carolina	100 + Citr	6.17	0.093	5.74
G200	N. Carolina	100 + Citr	5.37	0.118	6.32
G201	N. Carolina	100 + Citr	5.29	0.115	6.10
G202	N. Carolina	150 + Citr	6.41	0.082	5.24
G203	N. Carolina	150 + Citr	5.55	0.088	4.91
G204	N. Carolina	150 + Citr	6.02	0.082	4.92
G205	N. Carolina	200 + Citr	5.70	0.122	6.96
G206	N. Carolina	200 + Citr	5.26	0.110	5.77
G207	N. Carolina	200 + Citr	6.15	0.126	7.72
G208	Gafsa	50 + Citr	3.69	0.110	4.07
G209	Gafsa	50 + Citr	4.22	0.124	5.22
G210	Gafsa	50 + Citr	3.63	0.118	4.28
G211	Gafsa	100 + Citr	4.61	0.134	6.19
G212	Gafsa	100 + Citr	4.91	0.139	6.82
G213	Gafsa	100 + Citr	4.76	0.128	6.09
G214	Gafsa	150 + Citr	4.09	0.123	5.05
G215	Gafsa	150 + Citr	4.94	0.124	6.12
G216	Gafsa	150 + Citr	5.31	0.123	6.52

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G217	Gafsa	200 + Citr	5.31	0.149	7.93
G218	Gafsa	200 + Citr	5.30	0.135	7.14
G219	Gafsa	200 + Citr	5.39	0.121	6.52
G220	Tilemsi	50 + Citr	4.82	0.138	6.64
G221	Tilemsi	50 + Citr	4.94	0.105	5.21
G222	Tilemsi	50 + Citr	4.88	0.125	6.10
G223	Tilemsi	100 + Citr	6.14	0.125	7.69
G224	Tilemsi	100 + Citr	5.14	0.117	6.03
G225	Tilemsi	100 + Citr	4.40	0.129	5.67
G226	Tilemsi	150 + Citr	4.66	0.138	6.43
G227	Tilemsi	150 + Citr	4.52	0.129	5.85
G228	Tilemsi	150 + Citr	4.59	0.125	5.74
G229	Tilemsi	200 + Citr	5.22	0.118	6.16
G230	Tilemsi	200 + Citr	5.48	0.095	5.21
G231	Tilemsi	200 + Citr	4.96	0.106	5.28
G232	C. Florida	50 + Citr	3.74	0.111	4.16
G233	C. Florida	50 + Citr	3.66	0.120	4.38
G234	C. Florida	50 + Citr	3.68	0.104	3.84
G235	C. Florida	100 + Citr	5.96	0.117	6.96
G236	C. Florida	100 + Citr	4.75	0.111	5.30
G237	C. Florida	100 + Citr	6.13	0.107	6.58
G238	C. Florida	150 + Citr	6.41	0.112	7.19
G239	C. Florida	150 + Citr	4.40	0.132	5.81
G240	C. Florida	150 + Citr	4.37	0.125	5.45

Table 35. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G241	C. Florida	200 + Citr	6.92	0.112	7.72
G242	C. Florida	200 + Citr	5.30	0.132	6.99
G243	C. Florida	200 + Citr	4.63	0.134	6.19
G244	Hahotoe	50 + Citr	3.06	0.138	4.21
G245	Hahotoe	50 + Citr	3.40	0.113	3.83
G246	Hahotoe	50 + Citr	3.62	0.138	5.00
G247	Hahotoe	100 + Citr	4.98	0.125	6.21
G248	Hahotoe	100 + Citr	4.40	0.114	5.01
G249	Hahotoe	100 + Citr	2.73	0.138	4.21
G250	Hahotoe	150 + Citr	3.72	0.105	3.89
G251	Hahotoe	150 + Citr	3.88	0.131	5.08
G252	Hahotoe	150 + Citr	3.48	0.106	3.69
G253	Hahotoe	200 + Citr	4.22	0.106	4.49
G254	Hahotoe	200 + Citr	3.42	0.140	4.79
G255	Hahotoe	200 + Citr	3.91	0.086	3.38
G256	MCP	50	11.20	0.249	27.89
G257	MCP	50	10.64	0.239	25.44
G258	MCP	50	12.82	0.206	26.46
G259	MCP	100	12.55	0.281	35.27
G260	MCP	100	13.19	0.284	37.45
G261	MCP	100	12.19	0.279	33.98
G262	MCP	150	9.16	0.475	43.51
G263	MCP	150	11.01	0.387	42.64
G264	MCP	150	9.30	0.406	37.72
G265	MCP	200	10.40	0.576	59.88
G266	MCP	200	10.60	0.588	62.33
G267	MCP	200	10.80	0.573	61.86

Table 36. Dry matter yield, total P, and P yield of corn tops grown under greenhouse conditions on Clinton soil

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G1	None	Control	1.57	0.127	2.00
G2	None	Control	1.66	0.111	1.85
G3	None	Control	1.45	0.117	1.69
G4	None	Glass beads	1.42	0.093	1.32
G5	None	Glass beads	1.46	0.126	1.83
G6	None	Glass beads	1.95	0.097	1.88
G7	None	Glass beads	1.53	0.128	1.96
G8	None	Glass beads	1.44	0.120	1.73
G9	None	Glass beads	1.85	0.103	1.90
G10	None	Glass beads	1.47	0.123	1.80
G11	None	Glass beads	1.53	0.114	1.75
G12	None	Glass beads	1.50	0.120	1.80
G13	None	Glass beads	1.75	0.107	1.88
G14	None	Glass beads	1.51	0.100	1.50
G15	None	Glass beads	1.58	0.114	1.80
G88	None	Oxalic acid	1.88	0.081	1.53
G89	None	Oxalic acid	1.47	0.120	1.76
G90	None	Oxalic acid	2.14	0.089	1.91
G91	None	Oxalic acid	1.70	0.097	1.65
G92	None	Oxalic acid	1.37	0.090	1.24
G93	None	Oxalic acid	1.39	0.087	1.21
G94	None	Oxalic acid	1.70	0.099	1.69
G95	None	Oxalic acid	1.74	0.091	1.58
G96	None	Oxalic acid	1.41	0.109	1.54

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G97	None	Oxalic acid	1.95	0.097	1.89
G98	None	Oxalic acid	1.66	0.103	1.71
G99	None	Oxalic acid	1.78	0.110	1.96
G100	None	Citric acid	1.49	0.090	1.35
G101	None	Citric acid	1.63	0.087	1.42
G102	None	Citric acid	1.16	0.108	1.25
G103	None	Citric acid	1.53	0.083	1.27
G104	None	Citric acid	1.51	0.092	1.38
G105	None	Citric acid	1.55	0.095	1.47
G106	None	Citric acid	1.44	0.090	1.30
G107	None	Citric acid	1.41	0.083	1.18
G108	None	Citric acid	1.58	0.108	1.70
G109	None	Citric acid	1.14	0.113	1.28
G110	None	Citric acid	1.09	0.088	0.96
G111	None	Citric acid	1.78	0.084	1.50
G16	Kodjari	50	2.10	0.087	1.82
G17	Kodjari	50	1.63	0.123	2.01
G18	Kodjari	50	1.88	0.124	2.33
G19	Kodjari	100	2.08	0.122	2.53
G20	Kodjari	100	2.10	0.121	2.55
G21	Kodjari	100	2.05	0.118	2.41
G22	Kodjari	150	2.27	0.097	2.20
G23	Kodjari	150	1.76	0.119	2.09
G24	Kodjari	150	2.47	0.108	2.66

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G25	Kodjari	200	1.57	0.096	1.51
G26	Kodjari	200	2.47	0.098	2.42
G27	Kodjari	200	2.17	0.099	2.14
G28	N. Carolina	50	3.92	0.091	3.58
G29	N. Carolina	50	3.40	0.101	3.42
G30	N. Carolina	50	3.61	0.100	3.61
G31	N. Carolina	100	3.87	0.112	4.34
G32	N. Carolina	100	4.44	0.105	4.68
G33	N. Carolina	100	3.96	0.126	4.99
G34	N. Carolina	150	5.90	0.088	5.18
G35	N. Carolina	150	4.45	0.137	6.09
G36	N. Carolina	150	3.98	0.129	5.15
G37	N. Carolina	200	5.21	0.108	5.63
G38	N. Carolina	200	3.66	0.141	5.17
G39	N. Carolina	200	4.22	0.115	4.85
G40	Gafsa	50	4.12	0.082	3.38
G41	Gafsa	50	3.91	0.094	3.66
G42	Gafsa	50	3.28	0.096	3.14
G43	Gafsa	100	2.94	0.106	3.13
G44	Gafsa	100	4.42	0.127	5.61
G45	Gafsa	100	3.56	0.088	3.13
G46	Gafsa	150	3.49	0.110	3.83
G47	Gafsa	150	5.63	0.069	3.89
G48	Gafsa	150	4.10	0.115	4.71

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G49	Gafsa	200	4.19	0.075	3.14
G50	Gafsa	200	3.47	0.099	3.45
G51	Gafsa	200	4.16	0.104	4.33
G52	Tilemsi	50	1.87	0.086	1.61
G53	Tilemsi	50	3.29	0.049	1.60
G54	Tilemsi	50	2.39	0.085	2.04
G55	Tilemsi	100	2.36	0.130	3.07
G56	Tilemsi	100	3.13	0.136	4.25
G57	Tilemsi	100	2.41	0.140	3.37
G58	Tilemsi	150	2.65	0.151	4.01
G59	Tilemsi	150	2.55	0.130	3.25
G60	Tilemsi	150	2.65	0.126	3.33
G61	Tilemsi	200	4.48	0.113	5.05
G62	Tilemsi	200	3.72	0.111	4.14
G63	Tilemsi	200	3.44	0.115	3.96
G64	C. Florida	50	3.04	0.096	2.91
G65	C. Florida	50	3.16	0.082	2.60
G66	C. Florida	50	2.06	0.111	2.29
G67	C. Florida	100	3.30	0.099	3.28
G68	C. Florida	100	3.04	0.098	2.97
G69	C. Florida	100	3.85	0.116	4.46
G70	C. Florida	150	3.91	0.104	4.07
G71	C. Florida	150	3.73	0.117	4.37
G72	C. Florida	150	4.37	0.097	4.25

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G73	C. Florida	200	3.80	0.116	4.40
G74	C. Florida	200	3.11	0.101	3.13
G75	C. Florida	200	3.81	0.124	4.72
G76	Hahotoe	50	2.29	0.058	1.34
G77	Hahotoe	50	2.14	0.088	1.88
G78	Hahotoe	50	2.26	0.102	2.30
G79	Hahotoe	100	2.75	0.089	2.44
G80	Hahotoe	100	2.96	0.103	3.04
G81	Hahotoe	100	2.27	0.117	2.65
G82	Hahotoe	150	3.04	0.108	3.28
G83	Hahotoe	150	2.65	0.106	2.80
G84	Hahotoe	150	2.44	0.115	2.80
G85	Hahotoe	200	3.00	0.101	3.02
G86	Hahotoe	200	3.04	0.103	3.13
G87	Hahotoe	200	2.98	0.099	2.96
G112	Kodjari	50 + Oxal	1.86	0.090	1.68
G113	Kodjari	50 + Oxal	1.96	0.106	2.07
G114	Kodjari	50 + Oxal	1.81	0.123	2.23
G115	Kodjari	100 + Oxal	1.58	0.115	1.81
G116	Kodjari	100 + Oxal	2.16	0.120	2.59
G117	Kodjari	100 + Oxal	1.95	0.105	1.97
G118	Kodjari	150 + Oxal	2.51	0.096	2.41
G119	Kodjari	150 + Oxal	1.89	0.112	2.11
G120	Kodjari	150 + Oxal	2.46	0.089	2.20

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G121	Kodjari	200 + Oxal	2.61	0.106	2.77
G122	Kodjari	200 + Oxal	2.19	0.111	2.42
G123	Kodjari	200 + Oxal	2.05	0.115	2.36
G124	N. Carolina	50 + Oxal	3.90	0.118	4.59
G125	N. Carolina	50 + Oxal	3.52	0.111	3.92
G126	N. Carolina	50 + Oxal	3.20	0.118	3.76
G127	N. Carolina	100 + Oxal	3.70	0.126	4.66
G128	N. Carolina	100 + Oxal	3.78	0.110	4.16
G129	N. Carolina	100 + Oxal	3.87	0.094	3.65
G130	N. Carolina	150 + Oxal	3.91	0.107	4.19
G131	N. Carolina	150 + Oxal	4.13	0.108	4.44
G132	N. Carolina	150 + Oxal	4.03	0.118	4.74
G133	N. Carolina	200 + Oxal	3.83	0.114	4.35
G134	N. Carolina	200 + Oxal	4.11	0.119	4.90
G135	N. Carolina	200 + Oxal	4.91	0.110	5.41
G136	Gafsa	50 + Oxal	3.01	0.118	3.55
G137	Gafsa	50 + Oxal	3.52	0.118	4.14
G138	Gafsa	50 + Oxal	2.72	0.148	4.03
G139	Gafsa	100 + Oxal	4.36	0.096	4.17
G140	Gafsa	100 + Oxal	3.24	0.087	2.82
G141	Gafsa	100 + Oxal	3.80	0.111	4.22
G142	Gafsa	150 + Oxal	3.93	0.107	4.21
G143	Gafsa	150 + Oxal	3.80	0.129	4.90
G144	Gafsa	150 + Oxal	4.90	0.097	4.73

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G145	Gafsa	200 + Oxal	4.76	0.129	6.13
G146	Gafsa	200 + Oxal	4.66	0.122	5.66
G147	Gafsa	200 + Oxal	5.65	0.124	6.99
G148	Tilemsi	50 + Oxal	3.46	0.111	3.86
G149	Tilemsi	50 + Oxal	3.89	0.116	4.51
G150	Tilemsi	50 + Oxal	4.10	0.119	4.88
G151	Tilemsi	100 + Oxal	3.51	0.131	4.61
G152	Tilemsi	100 + Oxal	4.64	0.106	4.90
G153	Tilemsi	100 + Oxal	4.13	0.111	4.60
G154	Tilemsi	150 + Oxal	3.48	0.102	3.55
G155	Tilemsi	150 + Oxal	3.57	0.124	4.43
G156	Tilemsi	150 + Oxal	3.38	0.125	4.21
G157	Tilemsi	200 + Oxal	4.93	0.128	6.31
G158	Tilemsi	200 + Oxal	3.73	0.130	4.86
G159	Tilemsi	200 + Oxal	3.15	0.130	4.11
G160	C. Florida	50 + Oxal	2.92	0.114	3.34
G161	C. Florida	50 + Oxal	3.01	0.109	3.29
G162	C. Florida	50 + Oxal	2.26	0.113	2.55
G163	C. Florida	100 + Oxal	2.71	0.130	3.52
G164	C. Florida	100 + Oxal	3.16	0.119	3.77
G165	C. Florida	100 + Oxal	3.19	0.133	4.23
G166	C. Florida	150 + Oxal	4.01	0.120	4.82
G167	C. Florida	150 + Oxal	4.49	0.126	5.68
G168	C. Florida	150 + Oxal	3.54	0.126	4.48

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G169	C. Florida	200 + Oxal	4.23	0.143	6.06
G170	C. Florida	200 + Oxal	3.47	0.143	4.97
G171	C. Florida	200 + Oxal	4.29	0.117	5.03
G172	Hahotoe	50 + Oxal	2.60	0.131	3.41
G173	Hahotoe	50 + Oxal	2.32	0.121	2.80
G174	Hahotoe	50 + Oxal	2.30	0.115	2.65
G175	Hahotoe	100 + Oxal	2.10	0.127	2.66
G176	Hahotoe	100 + Oxal	2.10	0.128	2.66
G177	Hahotoe	100 + Oxal	3.63	0.116	4.21
G178	Hahotoe	150 + Oxal	3.51	0.110	3.86
G179	Hahotoe	150 + Oxal	3.46	0.102	3.54
G180	Hahotoe	150 + Oxal	3.19	0.122	3.89
G181	Hahotoe	200 + Oxal	3.07	0.118	3.61
G182	Hahotoe	200 + Oxal	3.69	0.085	3.13
G183	Hahotoe	200 + Oxal	3.83	0.109	4.17
G184	Kodjari	50 + Citr	2.16	0.085	1.84
G185	Kodjari	50 + Citr	2.32	0.088	2.04
G186	Kodjari	50 + Citr	2.22	0.072	1.60
G187	Kodjari	100 + Citr	2.09	0.095	1.98
G188	Kodjari	100 + Citr	1.88	0.115	2.17
G189	Kodjari	100 + Citr	2.27	0.089	2.03
G190	Kodjari	150 + Citr	2.40	0.105	2.52
G191	Kodjari	150 + Citr	2.81	0.092	2.59
G192	Kodjari	150 + Citr	2.95	0.093	2.74

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G193	Kodjari	200 + Citr	2.74	0.105	2.89
G194	Kodjari	200 + Citr	2.74	0.122	3.35
G195	Kodjari	200 + Citr	2.66	0.096	2.56
G196	N. Carolina	50 + Citr	3.79	0.134	5.08
G197	N. Carolina	50 + Citr	4.61	0.108	5.00
G198	N. Carolina	50 + Citr	4.53	0.103	4.68
G199	N. Carolina	100 + Citr	4.20	0.116	4.89
G200	N. Carolina	100 + Citr	5.01	0.094	4.72
G201	N. Carolina	100 + Citr	3.95	0.115	4.52
G202	N. Carolina	150 + Citr	4.72	0.121	5.69
G203	N. Carolina	150 + Citr	4.54	0.117	5.32
G204	N. Carolina	150 + Citr	4.37	0.107	4.69
G205	N. Carolina	200 + Citr	4.13	0.120	4.96
G206	N. Carolina	200 + Citr	4.79	0.106	5.08
G207	N. Carolina	200 + Citr	4.12	0.105	4.34
G208	Gafsa	50 + Citr	3.26	0.112	3.66
G209	Gafsa	50 + Citr	2.89	0.120	3.46
G210	Gafsa	50 + Citr	1.88	0.119	2.24
G211	Gafsa	100 + Citr	3.82	0.139	5.31
G212	Gafsa	100 + Citr	3.43	0.130	4.46
G213	Gafsa	100 + Citr	3.88	0.127	4.92
G214	Gafsa	150 + Citr	3.70	0.117	4.33
G215	Gafsa	150 + Citr	3.26	0.147	4.79
G216	Gafsa	150 + Citr	3.52	0.131	4.62

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G217	Gafsa	200 + Citr	3.94	0.112	4.40
G218	Gafsa	200 + Citr	3.99	0.133	5.31
G219	Gafsa	200 + Citr	3.42	0.144	4.92
G220	Tilemsi	50 + Citr	2.55	0.159	4.06
G221	Tilemsi	50 + Citr	3.26	0.116	3.78
G222	Tilemsi	50 + Citr	3.39	0.116	3.92
G223	Tilemsi	100 + Citr	3.89	0.098	3.82
G224	Tilemsi	100 + Citr	2.66	0.111	2.95
G225	Tilemsi	100 + Citr	3.50	0.123	4.31
G226	Tilemsi	150 + Citr	3.61	0.083	3.01
G227	Tilemsi	150 + Citr	2.41	0.142	3.42
G228	Tilemsi	150 + Citr	3.25	0.092	2.98
G229	Tilemsi	200 + Citr	3.57	0.125	4.45
G230	Tilemsi	200 + Citr	3.50	0.126	4.41
G231	Tilemsi	200 + Citr	3.57	0.112	3.99
G232	C. Florida	50 + Citr	3.43	0.102	3.51
G233	C. Florida	50 + Citr	3.38	0.102	3.45
G234	C. Florida	50 + Citr	3.00	0.116	3.48
G235	C. Florida	100 + Citr	4.00	0.122	4.90
G236	C. Florida	100 + Citr	3.77	0.120	4.54
G237	C. Florida	100 + Citr	3.50	0.123	4.30
G238	C. Florida	150 + Citr	4.50	0.116	5.22
G239	C. Florida	150 + Citr	4.70	0.096	4.52
G240	C. Florida	150 + Citr	4.60	0.111	5.09

Table 36. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G241	C. Florida	200 + Citr	4.50	0.108	4.87
G242	C. Florida	200 + Citr	4.72	0.105	4.97
G243	C. Florida	200 + Citr	4.07	0.125	5.10
G244	Hahotoe	50 + Citr	2.13	0.110	2.35
G245	Hahotoe	50 + Citr	2.65	0.097	2.58
G246	Hahotoe	50 + Citr	2.14	0.097	2.07
G247	Hahotoe	100 + Citr	2.43	0.086	2.09
G248	Hahotoe	100 + Citr	2.90	0.092	2.68
G249	Hahotoe	100 + Citr	2.58	0.115	2.96
G250	Hahotoe	150 + Citr	2.66	0.115	3.07
G251	Hahotoe	150 + Citr	3.33	0.110	3.67
G252	Hahotoe	150 + Citr	3.07	0.103	3.16
G253	Hahotoe	200 + Citr	3.80	0.105	3.99
G254	Hahotoe	200 + Citr	3.01	0.125	3.77
G255	Hahotoe	200 + Citr	3.44	0.099	3.40
G256	MCP	50	12.25	0.181	22.13
G257	MCP	50	11.94	0.146	17.39
G258	MCP	50	11.20	0.184	20.64
G259	MCP	100	11.40	0.271	30.89
G260	MCP	100	11.66	0.256	29.85
G261	MCP	100	11.19	0.300	33.58
G262	MCP	150	11.87	0.339	40.24
G263	MCP	150	11.59	0.394	45.72
G264	MCP	150	11.45	0.342	39.16
G265	MCP	200	9.57	0.357	34.20
G266	MCP	200	9.50	0.408	38.76
G267	MCP	200	9.41	0.383	36.06

Table 37. Dry matter yield, total P, and P yield of corn tops grown under greenhouse conditions on Grundy soil

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G1	None	Control	2.07	0.080	1.65
G2	None	Control	2.82	0.090	2.53
G3	None	Control	2.44	0.090	2.20
G4	None	Glass beads	1.50	0.107	1.60
G5	None	Glass beads	1.37	0.108	1.48
G6	None	Glass beads	1.60	0.114	1.82
G7	None	Glass beads	1.54	0.092	1.42
G8	None	Glass beads	2.00	0.090	1.81
G9	None	Glass beads	1.79	0.104	1.87
G10	None	Glass beads	1.88	0.101	1.91
G11	None	Glass beads	1.92	0.099	1.90
G12	None	Glass beads	1.79	0.112	2.00
G13	None	Glass beads	1.62	0.107	1.73
G14	None	Glass beads	1.44	0.096	1.38
G15	None	Glass beads	1.57	0.091	1.43
G88	None	Oxalic acid	2.29	0.121	2.76
G89	None	Oxalic acid	2.61	0.103	2.69
G90	None	Oxalic acid	2.84	0.076	2.15
G91	None	Oxalic acid	2.92	0.111	3.25
G92	None	Oxalic acid	2.55	0.081	2.06
G93	None	Oxalic acid	2.38	0.085	2.02
G94	None	Oxalic acid	2.36	0.105	2.48
G95	None	Oxalic acid	1.92	0.110	2.11
G96	None	Oxalic acid	2.81	0.104	2.94

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G97	None	Oxalic acid	2.68	0.096	2.57
G98	None	Oxalic acid	2.86	0.094	2.67
G99	None	Oxalic acid	3.05	0.086	2.63
G100	None	Citric acid	2.15	0.093	2.00
G101	None	Citric acid	2.44	0.119	2.91
G102	None	Citric acid	2.74	0.107	2.94
G103	None	Citric acid	2.13	0.093	1.97
G104	None	Citric acid	1.62	0.094	1.53
G105	None	Citric acid	1.81	0.089	1.60
G106	None	Citric acid	2.82	0.080	2.25
G107	None	Citric acid	2.65	0.083	2.21
G108	None	Citric acid	2.98	0.108	3.22
G109	None	Citric acid	2.64	0.072	1.89
G110	None	Citric acid	2.27	0.097	2.20
G111	None	Citric acid	2.32	0.100	2.32
G16	Kodjari	50	2.59	0.106	2.75
G17	Kodjari	50	1.92	0.112	2.16
G18	Kodjari	50	2.25	0.118	2.66
G19	Kodjari	100	2.00	0.119	2.38
G20	Kodjari	100	3.22	0.102	3.30
G21	Kodjari	100	2.55	0.096	2.44
G22	Kodjari	150	2.42	0.124	3.01
G23	Kodjari	150	2.37	0.127	3.00
G24	Kodjari	150	2.54	0.121	3.07

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G25	Kodjari	200	3.33	0.115	3.82
G26	Kodjari	200	2.17	0.118	2.57
G27	Kodjari	200	2.35	0.137	3.21
G28	N. Carolina	50	4.15	0.109	4.54
G29	N. Carolina	50	4.59	0.101	4.66
G30	N. Carolina	50	4.37	0.129	5.64
G31	N. Carolina	100	5.01	0.134	6.70
G32	N. Carolina	100	4.82	0.108	5.21
G33	N. Carolina	100	4.06	0.108	4.37
G34	N. Carolina	150	6.45	0.118	7.62
G35	N. Carolina	150	4.84	0.132	6.40
G36	N. Carolina	150	5.52	0.122	6.71
G37	N. Carolina	200	5.80	0.132	7.67
G38	N. Carolina	200	5.78	0.127	7.36
G39	N. Carolina	200	6.45	0.139	8.94
G40	Gafsa	50	3.99	0.118	4.70
G41	Gafsa	50	5.22	0.109	5.69
G42	Gafsa	50	4.22	0.143	6.04
G43	Gafsa	100	4.10	0.108	4.41
G44	Gafsa	100	4.01	0.131	5.26
G45	Gafsa	100	5.53	0.110	6.08
G46	Gafsa	150	5.66	0.120	6.81
G47	Gafsa	150	5.06	0.125	6.30
G48	Gafsa	150	6.27	0.129	8.12

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G49	Gafsa	200	5.29	0.131	6.91
G50	Gafsa	200	5.27	0.144	7.58
G51	Gafsa	200	4.58	0.140	6.42
G52	Tilemsi	50	3.54	0.123	4.35
G53	Tilemsi	50	3.72	0.121	4.51
G54	Tilemsi	50	4.51	0.128	5.78
G55	Tilemsi	100	5.49	0.113	6.19
G56	Tilemsi	100	4.14	0.138	5.79
G57	Tilemsi	100	4.45	0.116	5.16
G58	Tilemsi	150	3.79	0.150	5.68
G59	Tilemsi	150	3.68	0.130	4.79
G60	Tilemsi	150	3.90	0.135	5.26
G61	Tilemsi	200	4.35	0.138	6.02
G62	Tilemsi	200	4.21	0.139	5.85
G63	Tilemsi	200	4.28	0.114	4.88
G64	C. Florida	50	4.29	0.114	4.87
G65	C. Florida	50	4.25	0.141	6.01
G66	C. Florida	50	4.27	0.112	4.78
G67	C. Florida	100	5.03	0.137	6.91
G68	C. Florida	100	3.16	0.132	4.16
G69	C. Florida	100	3.18	0.162	5.15
G70	C. Florida	150	4.10	0.112	4.58
G71	C. Florida	150	4.27	0.104	4.42
G72	C. Florida	150	4.18	0.131	5.48

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G73	C. Florida	200	4.14	0.128	5.30
G74	C. Florida	200	4.45	0.116	5.16
G75	C. Florida	200	4.30	0.128	5.50
G76	Hahotoe	50	2.04	0.132	2.69
G77	Hahotoe	50	3.10	0.121	3.75
G78	Hahotoe	50	3.81	0.096	3.66
G79	Hahotoe	100	3.66	0.125	4.58
G80	Hahotoe	100	3.52	0.119	4.19
G81	Hahotoe	100	4.24	0.121	5.13
G82	Hahotoe	150	3.91	0.108	4.24
G83	Hahotoe	150	4.41	0.128	5.63
G84	Hahotoe	150	3.40	0.111	3.78
G85	Hahotoe	200	4.25	0.130	5.52
G86	Hahotoe	200	4.22	0.142	5.99
G87	Hahotoe	200	4.79	0.123	5.91
G112	Kodjari	50 + Oxal	1.92	0.116	2.23
G113	Kodjari	50 + Oxal	2.25	0.083	1.88
G114	Kodjari	50 + Oxal	1.60	0.104	1.66
G115	Kodjari	100 + Oxal	2.55	0.108	2.76
G116	Kodjari	100 + Oxal	2.34	0.128	3.00
G117	Kodjari	100 + Oxal	2.14	0.133	2.84
G118	Kodjari	150 + Oxal	3.16	0.126	3.99
G119	Kodjari	150 + Oxal	2.85	0.118	3.36
G120	Kodjari	150 + Oxal	2.12	0.147	3.11

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G121	Kodjari	200 + Oxal	3.32	0.132	4.39
G122	Kodjari	200 + Oxal	2.65	0.132	3.50
G123	Kodjari	200 + Oxal	3.22	0.121	3.89
G124	N. Carolina	50 + Oxal	3.88	0.140	5.43
G125	N. Carolina	50 + Oxal	3.79	0.154	5.84
G126	N. Carolina	50 + Oxal	3.97	0.141	5.59
G127	N. Carolina	100 + Oxal	6.36	0.147	6.42
G128	N. Carolina	100 + Oxal	4.05	0.112	4.53
G129	N. Carolina	100 + Oxal	4.68	0.113	5.28
G130	N. Carolina	150 + Oxal	6.81	0.113	7.70
G131	N. Carolina	150 + Oxal	5.64	0.169	9.54
G132	N. Carolina	150 + Oxal	6.22	0.148	9.20
G133	N. Carolina	200 + Oxal	6.99	0.142	9.94
G134	N. Carolina	200 + Oxal	6.41	0.135	8.65
G135	N. Carolina	200 + Oxal	5.83	0.149	8.67
G136	Gafsa	50 + Oxal	4.85	0.145	5.31
G137	Gafsa	50 + Oxal	3.72	0.140	5.22
G138	Gafsa	50 + Oxal	3.61	0.170	6.14
G139	Gafsa	100 + Oxal	5.47	0.121	6.62
G140	Gafsa	100 + Oxal	5.46	0.118	6.42
G141	Gafsa	100 + Oxal	5.46	0.131	6.18
G142	Gafsa	150 + Oxal	5.78	0.127	7.34
G143	Gafsa	150 + Oxal	5.72	0.129	7.41
G144	Gafsa	150 + Oxal	6.15	0.131	8.07

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G145	Gafsa	200 + Oxal	6.34	0.101	6.41
G146	Gafsa	200 + Oxal	7.39	0.114	8.40
G147	Gafsa	200 + Oxal	5.00	0.147	7.35
G148	Tilemsi	50 + Oxal	4.53	0.101	4.58
G149	Tilemsi	50 + Oxal	5.66	0.101	5.72
G150	Tilemsi	50 + Oxal	5.37	0.115	6.17
G151	Tilemsi	100 + Oxal	5.75	0.086	4.92
G152	Tilemsi	100 + Oxal	4.42	0.124	5.47
G153	Tilemsi	100 + Oxal	4.40	0.127	5.72
G154	Tilemsi	150 + Oxal	7.47	0.119	8.90
G155	Tilemsi	150 + Oxal	6.72	0.124	8.33
G156	Tilemsi	150 + Oxal	5.96	0.138	8.22
G157	Tilemsi	200 + Oxal	5.23	0.136	7.11
G158	Tilemsi	200 + Oxal	5.31	0.153	8.10
G159	Tilemsi	200 + Oxal	5.12	0.120	6.13
G160	C. Florida	50 + Oxal	4.37	0.119	5.19
G161	C. Florida	50 + Oxal	4.43	0.132	5.84
G162	C. Florida	50 + Oxal	5.67	0.117	6.65
G163	C. Florida	100 + Oxal	5.30	0.135	7.14
G164	C. Florida	100 + Oxal	5.99	0.119	7.15
G165	C. Florida	100 + Oxal	5.99	0.138	8.28
G166	C. Florida	150 + Oxal	6.53	0.123	8.02
G167	C. Florida	150 + Oxal	6.20	0.123	7.61
G168	C. Florida	150 + Oxal	6.36	0.133	8.46

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G169	C. Florida	200 + Oxal	5.46	0.138	7.53
G170	C. Florida	200 + Oxal	5.94	0.129	7.64
G171	C. Florida	200 + Oxal	4.97	0.138	6.86
G172	Hahotoe	50 + Oxal	3.29	0.107	3.51
G173	Hahotoe	50 + Oxal	3.27	0.123	4.02
G174	Hahotoe	50 + Oxal	2.46	0.135	3.31
G175	Hahotoe	100 + Oxal	2.69	0.126	3.40
G176	Hahotoe	100 + Oxal	2.91	0.133	3.86
G177	Hahotoe	100 + Oxal	3.79	0.151	5.74
G178	Hahotoe	150 + Oxal	4.33	0.125	5.41
G179	Hahotoe	150 + Oxal	3.52	0.125	4.39
G180	Hahotoe	150 + Oxal	4.32	0.128	5.51
G181	Hahotoe	200 + Oxal	4.62	0.140	6.47
G182	Hahotoe	200 + Oxal	5.17	0.124	6.39
G183	Hahotoe	200 + Oxal	4.07	0.147	5.99
G184	Kodjari	50 + Citr	1.75	0.126	2.21
G185	Kodjari	50 + Citr	2.29	0.081	1.86
G186	Kodjari	50 + Citr	1.91	0.118	2.25
G187	Kodjari	100 + Citr	2.59	0.118	3.07
G188	Kodjari	100 + Citr	2.50	0.094	2.35
G189	Kodjari	100 + Citr	2.92	0.100	2.93
G190	Kodjari	150 + Citr	3.62	0.112	4.05
G191	Kodjari	150 + Citr	3.46	0.123	4.26
G192	Kodjari	150 + Citr	2.69	0.127	3.41

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G193	Kodjari	200 + Citr	3.69	0.150	5.52
G194	Kodjari	200 + Citr	3.72	0.106	3.93
G195	Kodjari	200 + Citr	3.74	0.114	4.27
G196	N. Carolina	50 + Citr	5.19	0.132	6.86
G197	N. Carolina	50 + Citr	4.18	0.149	6.21
G198	N. Carolina	50 + Citr	5.40	0.111	6.00
G199	N. Carolina	100 + Citr	4.90	0.151	7.40
G200	N. Carolina	100 + Citr	5.85	0.133	7.75
G201	N. Carolina	100 + Citr	6.92	0.117	8.07
G202	N. Carolina	150 + Citr	5.36	0.134	7.17
G203	N. Carolina	150 + Citr	7.69	0.106	8.15
G204	N. Carolina	150 + Citr	6.14	0.108	6.64
G205	N. Carolina	200 + Citr	4.04	0.1455.85	
G206	N. Carolina	200 + Citr	5.27	0.1427.48	
G207	N. Carolina	200 + Citr	4.66	0.146	6.80
G208	Gafsa	50 + Citr	4.44	0.135	6.01
G209	Gafsa	50 + Citr	3.00	0.147	4.40
G210	Gafsa	50 + Citr	4.02	0.131	5.28
G211	Gafsa	100 + Citr	5.58	0.126	7.02
G212	Gafsa	100 + Citr	5.55	0.136	7.54
G213	Gafsa	100 + Citr	3.73	0.169	6.31
G214	Gafsa	150 + Citr	4.80	0.143	6.86
G215	Gafsa	150 + Citr	4.87	0.129	6.28
G216	Gafsa	150 + Citr	5.86	0.115	6.77

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G217	Gafsa	200 + Citr	4.89	0.157	7.67
G218	Gafsa	200 + Citr	4.24	0.149	6.32
G219	Gafsa	200 + Citr	4.56	0.128	5.84
G220	Tilemsi	50 + Citr	3.95	0.110	4.34
G221	Tilemsi	50 + Citr	3.78	0.107	4.04
G222	Tilemsi	50 + Citr	4.54	0.115	5.24
G223	Tilemsi	100 + Citr	3.16	0.153	4.84
G224	Tilemsi	100 + Citr	3.28	0.133	4.36
G225	Tilemsi	100 + Citr	4.93	0.128	6.32
G226	Tilemsi	150 + Citr	4.79	0.131	6.29
G227	Tilemsi	150 + Citr	5.03	0.124	6.24
G228	Tilemsi	150 + Citr	5.27	0.120	6.31
G229	Tilemsi	200 + Citr	4.69	0.142	6.66
G230	Tilemsi	200 + Citr	4.69	0.109	5.13
G231	Tilemsi	200 + Citr	4.02	0.160	6.44
G232	C. Florida	50 + Citr	3.56	0.120	4.26
G233	C. Florida	50 + Citr	3.62	0.112	4.05
G234	C. Florida	50 + Citr	3.67	0.135	4.95
G235	C. Florida	100 + Citr	5.00	0.128	6.38
G236	C. Florida	100 + Citr	5.62	0.118	6.61
G237	C. Florida	100 + Citr	5.36	0.115	6.19
G238	C. Florida	150 + Citr	5.04	0.128	6.45
G239	C. Florida	150 + Citr	5.83	0.122	7.10
G240	C. Florida	150 + Citr	4.25	0.135	5.74

Table 37. (Continued)

Pot #	Phosphate rock added	Treatment	Dry matter	Total P	Yield of P
		mg P kg^{-1} soil	g pot^{-1}	%	mg pot^{-1}
G241	C. Florida	200 + Citr	4.57	0.164	7.52
G242	C. Florida	200 + Citr	5.01	0.140	7.04
G243	C. Florida	200 + Citr	4.79	0.139	6.66
G244	Hahotoe	50 + Citr	3.27	0.122	4.00
G245	Hahotoe	50 + Citr	2.96	0.117	3.47
G246	Hahotoe	50 + Citr	2.88	0.127	3.65
G247	Hahotoe	100 + Citr	3.53	0.126	4.45
G248	Hahotoe	100 + Citr	3.50	0.113	3.95
G249	Hahotoe	100 + Citr	3.50	0.127	4.45
G250	Hahotoe	150 + Citr	3.73	0.122	4.55
G251	Hahotoe	150 + Citr	3.26	0.112	3.66
G252	Hahotoe	150 + Citr	3.50	0.111	3.88
G253	Hahotoe	200 + Citr	3.93	0.143	5.60
G254	Hahotoe	200 + Citr	4.00	0.136	5.46
G255	Hahotoe	200 + Citr	4.55	0.126	5.75
G256	MCP	50	11.98	0.184	22.01
G257	MCP	50	12.11	0.218	26.40
G258	MCP	50	12.40	0.249	30.90
G259	MCP	100	12.50	0.308	38.50
G260	MCP	100	13.98	0.266	37.19
G261	MCP	100	12.86	0.297	38.22
G262	MCP	150	12.14	0.310	37.65
G263	MCP	150	12.12	0.351	42.57
G264	MCP	150	12.10	0.327	39.57
G265	MCP	200	12.37	0.371	45.90
G266	MCP	200	11.88	0.374	44.44
G267	MCP	200	13.28	0.391	51.90

Table 38. Effect of sources and rates of phosphate rock mixed with oxalic acid on dry matter yield of corn top produced on three soils

	Dry matter yield at rate (mg) of P application per pot of soil specified											
	Gosport soil				Clinton soil				Grundy soil			
Phosphate rock	50	100	150	200	50	100	150	200	50	100	150	200
	g pot^{-1}											
Kodjari	1.4	1.3	2.1	3.1	1.9	1.9	2.3	2.3	1.9	2.3	2.7	3.1
North Carolina	4.4	4.5	6.8	7.5	3.5	3.8	4.0	4.3	3.9	5.0	6.2	6.4
Gafsa	4.6	5.3	6.2	5.4	3.1	3.8	4.2	5.0	4.1	5.5	5.9	6.2
Tilemsi Valley	4.3	5.4	5.3	5.4	3.8	4.1	3.5	3.9	5.2	4.8	6.7	5.2
Central Florida	3.6	4.8	5.1	5.5	2.7	3.0	4.0	4.0	4.8	5.8	6.4	5.4
Hahotoe	2.3	2.8	4.4	4.6	2.4	2.6	3.4	3.5	3.0	3.1	4.0	4.6
LSD $p < 0.05$	0.6	0.7	0.6	0.4	0.6	0.9	0.6	1.0	0.9	1.2	0.9	1.1

Table 39. Effect of sources and rates of phosphate rock mixed with citric acid on dry matter yield of corn top produced on three soils

	Dry matter yield at rate (mg) of P application per pot of soil specified											
	Gosport soil				Clinton soil				Grundy soil			
Phosphate rock	50	100	150	200	50	100	150	200	50	100	150	200
	g pot^{-1}											
Kodjari	1.2	2.0	2.3	2.8	2.2	2.1	2.7	2.7	2.0	2.7	3.2	3.2
North Carolina	3.8	5.6	6.0	5.7	4.3	4.4	4.5	4.3	4.9	5.9	6.4	4.6
Gafsa	3.8	4.8	4.8	5.3	2.7	3.7	3.5	3.8	3.8	4.9	5.2	4.6
Tilemsi Valley	4.9	5.2	4.6	5.2	3.1	3.4	3.1	3.5	4.1	3.8	5.0	4.5
Central Florida	3.7	5.6	5.1	5.6	3.3	3.8	4.6	4.4	3.6	5.3	5.0	4.8
Hahotoe	3.4	4.0	3.7	3.8	2.3	2.6	30	3.4	3.0	2.7	3.5	4.2
LSD $p < 0.05$	0.4	1.3	1.0	1.0	0.8	0.7	0.6	0.5	0.8	1.3	1.2	0.6

Table 40. Effect of sources and rates of phosphate rock mixed with oxalic acid on P yield of corn top produced on three soils

Phosphate rock	Phosphorus yield at rate (mg) of P application per pot of soil specified											
	Gosport soil				Clinton soil				Grundy soil			
	50	100	150	200	50	100	150	200	50	100	150	200
	mg pot^{-1}											
Kodjari	1.4	1.7	2.5	3.7	2.0	2.1	2.2	2.5	1.9	2.9	3.5	3.9
North Carolina	5.2	5.8	7.1	10.1	4.1	4.1	4.4	4.9	5.6	5.4	8.8	9.1
Gafsa	5.9	6.5	7.6	6.8	3.9	3.7	4.6	6.3	5.6	6.4	7.6	7.4
Tilemsi Valley	5.0	6.4	5.7	7.5	4.4	4.7	4.1	5.1	5.5	5.4	8.5	7.1
Central Florida	5.0	5.0	5.6	6.1	3.1	3.8	5.0	5.4	5.9	7.5	8.0	7.3
Hahotoe	2.9	2.8	3.7	5.5	3.0	3.2	3.8	3.6	3.6	4.3	5.1	6.3
LSD $p < 0.05$	1.0	1.1	1.3	1.1	0.7	1.0	0.7	1.2	1.0	1.3	1.0	1.2

Table 41. Effect of sources and rates of phosphate rock mixed with citric acid on P yield of corn top produced on three soils

	Phosphorus yield at rate (mg) of P application per pot of soil specified											
	Gosport soil				Clinton soil				Grundy soil			
Phosphate rock	50	100	150	200	50	100	150	200	50	100	150	200
	mg pot^{-1}											
Kodjari	1.3	2.4	2.8	2.8	1.8	2.1	2.6	2.9	2.1	2.8	3.9	4.6
North Carolina	3.9	6.0	5.0	6.8	4.9	4.7	5.2	4.8	6.4	7.7	7.3	6.7
Gafsa	4.5	6.4	5.9	7.2	3.1	4.9	4.6	4.9	5.2	7.0	6.6	6.6
Tilemsi Valley	6.0	6.5	5.6	5.6	3.9	3.7	3.1	4.3	4.5	5.2	6.3	6.1
Central Florida	4.1	6.3	6.2	7.0	3.5	4.6	4.9	5.0	4.4	6.4	6.4	7.1
Hahotoe	4.3	5.1	4.2	4.2	2.3	2.6	3.3	3.7	3.7	4.3	4.0	5.6
LSD $p < 0.05$	0.9	1.3	1.2	1.2	0.6	0.7	0.6	0.6	0.9	1.0	0.9	1.3